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# Effect of solvent on radical cyclisation pathways: $S_{RN}1$ *vs.* aryl-aryl bond forming mechanisms

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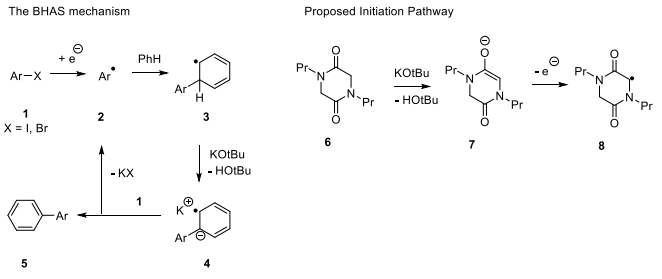
A recent paper identified a series of alternative cyclisation pathways of aryl radicals that resulted from electron transfer to various tethered haloarene–acetylarene substrates, in either benzene or DMSO as solvent. The electron transfer occurred from one of two enolates that were formed in the presence of KOtBu: either the enolate of the acetylarene, within the haloarene–acetylarene substrate, or the enolate **7** of the *N,N'*-dipropyl diketopiperazine (DKP) additive **6**. This paper uses contemporary computational methods to determine the reaction pathways involved; depending on the substrate, the aryl radical underwent (i) $S_{RN}1$ onto the enolate anion of the acetylarene, (ii) aryl-aryl bond formation, (iii) tandem hydrogen atom abstraction followed by $S_{RN}1$ cyclisation and even (iv) ArC-N cleavage. The influence of the solvent was investigated. In this paper it is shown that the solvent influences which reactive species are present in the reaction mixture, and whether each species acts as an electron donor or an electron acceptor in the radical initiation or propagation steps. The main initiation step is a single electron transfer from the enolate anion **7** of the DKP additive in benzene, but in DMSO the initiation can occur from the enolate anion of the substrate itself. Using computational techniques a deeper understanding of the radical pathways involved has been obtained, which shows how we can use solvent to preferentially access products arising from either $S_{RN}1$ or aryl-aryl bond formation pathways.

## Introduction

The reaction conditions (temperature, pH, solvent, etc.) have a significant effect on both the viability and products of reactions. The choice of solvent affects the chemical reactivity by influencing many factors, such as the rate of reaction (stabilisation of the transition state relative to the starting materials) and the equilibrium (relative stability of the reactants and products), such that changing the solvent may change the preference for competing pathways.[1-5]

There has been a recent resurgence in the use of radical chemistry within organic synthesis.[6-12] As part of the resurgence, the transition metal-free formation of biaryl compounds has received increased attention. Typically, these processes involve a haloarene that couples to an aromatic ring, commonly benzene, in the presence of KOtBu and an additive such as *N,N'*-dipropyl diketopiperazine (DKP), **6**.[13-18] Benzene and pyridine are the most common solvents used in these reactions as they are the coupling partner for the aryl halide in the reactions, and high temperatures are employed to achieve efficient coupling.[13,15-21] The mechanism by which these coupling reactions occur involves initiation of the reaction *via* a single electron transfer (SET) to the haloarene **1** to form an aryl radical **2**. This aryl radical **2** then attacks a benzene ring in a base-promoted homolytic aromatic substitution (BHAS) mechanism to form **4** upon deprotonation (Scheme 1).[14] This radical anion **4** propagates the radical chain to yield the product **5** and a new aryl radical **2**. The SET is proposed to occur from an electron donor, such as the enolate anion **7**, which is formed *in situ* from the reaction of KOtBu and an organic additive such as DKP **6**. Alternative partners than benzene have also been shown to couple to the aryl radical **2**, such as alkenes, and carbon monoxide, while enolate anions can undergo coupling to aryl radicals through an $S_{RN}1$ reaction.[20-30] Most of these couplings were performed in benzene,[13-22] however it has also been shown that $S_{RN}1$ coupling to enolate anions can be achieved efficiently in DMSO at room temperature.[26,30]




**Scheme 1.** In the BHAS mechanism, the rate determining step is the SET from an electron donor **7**, formed *in situ*, to the haloarene **1**

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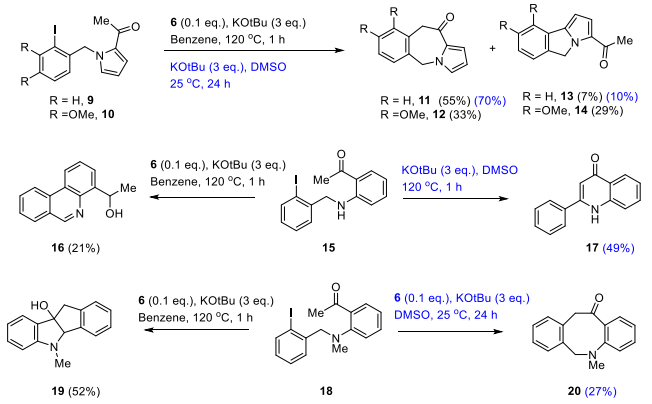



**Scheme 2.** The products from SET to **9**, **10**, **15** and **18** in benzene (black) or DMSO (blue)

Recent studies in the Murphy laboratory have demonstrated the influence that solvent can have on the cyclisation of an aryl radical onto complex enolate anions, initiated in the ground-state by an additive, DKP **6**.[31] (This followed a similar study by Rossi *et al.* who used photoactivation to initiate these cyclisations.) [32] It was observed that on changing the solvent from benzene to DMSO, the radical cyclisation could be performed at lower temperatures, and in some instances the favoured reaction pathway was changed, resulting in a different product distribution (Scheme 2). The observed strong solvent dependence of these results suggests that these systems represent an excellent case study to probe the various competitive reaction mechanisms and identify what effect the solvent had on these radical cyclisations, as well as specifying the initiation and propagation steps. Through this process, we identify several approaches to tune the reactivity and manipulate the product outcomes by controlling the reaction environment.

## Results and Discussion

### Methods

The calculations were run using the M06-2X functional[33-34] with the 6-311++G(d,p) basis set[35-39] on all atoms, except for the iodine. Iodine was modelled with the MWB46 relativistic pseudo potential and associated basis set.[40] All calculations were carried out using the C-PCM implicit solvent model[41-42] with the dielectric constant for benzene (ε=2.2706) or DMSO (ε=46.826) as appropriate. All calculations were performed in Gaussian09.[43] After optimisation, all equilibrium structures were subjected to a frequency calculation to characterize the optimized structures as minima or transition states, where the transition states were found to each have a single imaginary frequency. In addition, the vibrational frequencies were used to obtain temperature corrected (298.15 K) energies, enthalpies, entropies, and free energies

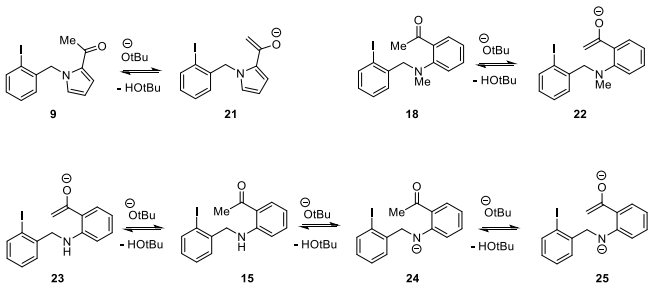
### The Initiation Step

In the presence of KOtBu the substrates **9**, **15** and **18** are present in equilibrium with their deprotonated forms (Scheme 3). However, the position of this equilibrium will depend upon the reaction environment and, in particular, on the choice of solvent. The energetic barrier, $\Delta G^*$, and the relative energies between the starting material and products, $\Delta G_{rxn}$, for the deprotonation of the substrates **9**, **15** and **18** by KOtBu, in both DMSO and benzene, are displayed in Table 1.

The results show that under the basic reaction conditions, the substrates **9** and **18** will predominantly exist as their respective enolate anions **21** and **22**, in both benzene and DMSO. It should be noted that the deprotonation of **10** was not modeled since it has a very similar structure to **9**. In the deprotonation of substrate **15**, the solvent is playing a key role in differentiating the major species present in the reaction mixture. That is, **15** can potentially form three deprotonated species that may all be present in equilibrium, which are the enolate anion **23**, the N-deprotonated species **24** and the doubly deprotonated enolate anionic species **25**. In benzene, the major species present in the reaction mixture will be **24**, whereas in DMSO the major species will be **25**, as displayed in Scheme 3.

There are different possible ways that these substrates, represented by a generic molecule **26**, could form the cyclized products under the ground-state conditions in the presence of a base (Scheme 4):

1. The benzyne formation pathway.[44] The base would react with




**Scheme 3.** The various deprotonation states of the substrates **9**, **15** and **18**

**Table 1.** The energetics for the deprotonation of substrates **9**, **15** and **18** in the presence of the butoxide anion (OtBu), in both benzene and DMSO

| Equilibrium [a] | Benzene $\Delta G^*$ (kcal/mol) | Benzene $\Delta G_{rxn}$ (kcal/mol) | DMSO $\Delta G^*$ (kcal/mol) | DMSO $\Delta G_{rxn}$ (kcal/mol) |
|---|---|---|---|---|
| **9** – **21** [**21** – **9**] | + 2.5 [+ 8.0] | - 5.5 | + 2.2 [+ 10.8] | - 8.6 |
| **15** – **23** [**23** – **15**] | + 1.8 [+ 9.9] | - 8.1 | + 1.5 [+ 11.8] | - 10.3 |
| **15** – **24** [**24** – **15**] | 0.0 [+ 9.0] | - 9.0 | 0.0 [+ 10.4] | - 10.4 |
| **24** – **25** [**25** – **24**] | + 4.5 [+ 1.0] | + 3.5 | + 4.7 [+ 9.8] | - 5.1 |
| **18** – **22** [**22** – **18**] | + 1.0 [+ 11.0] | - 10.0 | + 1.2 [+ 10.7] | - 9.5 |

[a] The equilibrium was also calculated using KOtBu (Supporting Information, Figure S1).

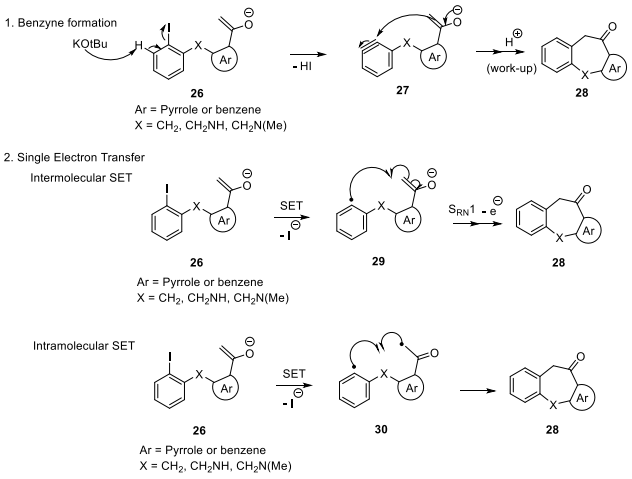
substrate **26**, to deprotonate the proton *ortho* to the iodine and therefore eliminate HI and form a benzyne intermediate **27**. Cyclisation of the enolate onto the benzyne yields **28** upon protonation during work-up.

2. Intermolecular SET to the haloaryl moiety of **26** would yield the aryl radical **29** upon loss of the iodide anion (initiation). The aryl radical would cyclise onto the enolate *via* an $S_{RN}1$ mechanism to yield **28** upon loss of an electron (propagation).

3. Another possibility is intramolecular SET, from the enolate anion to the haloaryl moiety, which will form intermediate **30**. Radical recombination will lead to the product **28**.[45,32] Experimentally it was shown that substrate **10**, which can only be activated by SET and is incapable of undergoing benzyne formation, was able to cyclise to form **12** and **14**, albeit with lower product yields than the cyclisation of **9**.[31,46] Therefore SET is implicated in the conversion of substrates **9**, **15** and **18** to form the aryl radical, like **29**. However, in view of the lower yield from substrate **10**, we did not immediately rule out the benzyne mechanism contributing to these results in appropriate substrates. Therefore we modelled the benzyne formation pathway from **21** in DMSO (Supporting Information, Scheme S1.3). The formation of the benzyne intermediate from **21** was calculated to be unfavourable, with a Gibbs free energy, $\Delta G_{rxn}$ = 18.4 kcal/mol. Although this benzyne formation is an endergonic reaction pathway, the calculated $\Delta G_{rxn}$ would be accessible at room temperature in DMSO (Supporting Information, Scheme S1.3). Furthermore the cyclisation of the enolate anion onto the benzyne intermediate to form the product **11** was calculated to be barrierless and exergonic, $\Delta G_{rxn}$ = -53.9 kcal/mol. This suggests that the benzyne pathway may contribute to the formation in **11** in DMSO, albeit as a minor pathway.

The reactive species that are susceptible to an initiation by SET were identified by analysis of the LUMOs of the neutral substrates and their respective deprotonated species (Supporting Information, Table S1.3). For **21**, **23**, **24**, **22** and the enolate anion of **10**, the LUMOs reside on the C-I σ* in both benzene and DMSO. Therefore SET to these species will give cleavage of the C-I bond and the formation of the aryl radical, analogous to **29** or **30** (depending on whether the SET was intermolecular or intramolecular). For the neutral species **9** the LUMO is delocalized over the molecule, partly residing on both the C-I σ* and the haloaryl π* orbitals.[47-49] Interestingly the LUMO of the doubly-deprotonated species **25** was different in the two solvents. In DMSO the LUMO resided on the C-I σ* orbital, whereas in benzene the LUMO did not reside on the C-I σ*, and it was actually the LUMO+2 orbital that did. Murphy *et al.* proposed that the electron donor is the enolate anion of the DKP additive, **7**, or, in some cases, the enolate anion of the substrates themselves, such as **21**, **22** or **25**. Therefore, the HOMOs of the enolate anion of DKP **7** and the enolate anions of the substrates were analysed and, as expected, they reside on the electron-rich enolate anion moieties (Supporting Information, Table S1.3).[16,31]

To determine whether the enolate anion of DKP **7** is the electron donor, or whether the enolate anions present in the substrates themselves donate an electron, the energetics for the single




**Scheme 4.** Possible initiation pathways for the cyclisation of the substrates (applicable to substrates **9**, **15** and **18**)

electron transfer were calculated.[50,51-53] We investigated the Gibbs free energy profile, both the barrier, $\Delta G^*$, and the relative energy, $\Delta G_{rxn}$, for SET using Marcus Hush theory[54] in our model systems considering the different polarising ability of the benzene and DMSO solvent *via* the C-PCM implicit solvent model.

In benzene, SET from **7** to **21**, (the enolate of **9**) has an energetic barrier of 34.3 kcal/mol, whereas in DMSO the barrier for SET is much lower, 22.7 kcal/mol (Table 2 and Supporting Information, Table S1.6). Therefore by changing the solvent from benzene to DMSO, a lower energetic barrier is obtained, which is accessible at room temperature. Experimentally it was shown that the reaction can proceed at room temperature with DKP additive in DMSO (forms **11** in 76%) but not in benzene.[31] It was then investigated whether the enolate anion **21** could act as an electron donor to another molecule of **21**.

**Table 2.** The $\Delta G^*$ and $\Delta G_{rxn}$ for SET to the substrates **9**, **10**, **15** and **18**, from either **7** or the enolate anions **21**, **23**, **22** and the enolate anion of **10**, in both benzene and DMSO

| Electron Acceptor | Electron Donor | Benzene $\Delta G^*$ / $\Delta G_{rxn}$ (kcal/mol) | DMSO $\Delta G^*$ / $\Delta G_{rxn}$ (kcal/mol) |
|---|---|---|---|
| **21** [a] | **7** | 34.3 / 24.7 | 22.7 / 10.4 |
| **21** [a] | **21** | 45.8 / 42.5 | 33.0 / 27.8 |
| **24** | **7** | 38.7 / 34.3 | 23.3 / 11.4 |
| **24** | **25** | 18.4 / 6.2 | 20.7 / 10.1 |
| **22** | **7** | 31.7 / 23.1 | 22.3 / 10.8 |
| **22** | **22** | 43.3 / 40.1 | 31.0 / 26.5 |
| Enolate Anion of **10** [a] | **7** | 33.9 / 25.3 | 22.6 / 9.8 |
| Enolate Anion of **10** [a] | Enolate Anion of **10** | 45.0 / 41.3 | 32.0 / 25.6 |

[a] SET to the neutral species was also calculated using **7** (Supporting Information Table S1.6). [b] The energetics were not calculated.

In DMSO SET from **21** to **21** has an energetic barrier of 33.0 kcal/mol, which is feasible at high temperatures, however in benzene the barrier is 45.8 kcal/mol which is not accessible. This trend was also observed experimentally.[55,56] Therefore by changing the solvent from benzene to DMSO the reaction can proceed efficiently in the absence of DKP.[57] The substrates **18** and **10** show a similar pattern to **9**. This has demonstrated that the solvent has a large influence on the initiation step in the formation of the aryl radical, and that changing the reaction solvent to DMSO enables the initiation step to proceed under milder reaction conditions.[58] It also shows that by changing solvents, from benzene to DMSO, it increases the strength of the electron donation from the enolate anions of the substrates themselves, and thus in DMSO the reaction will proceed by SET from the enolate anions of the substrates, without the need for the DKP additive **6**.

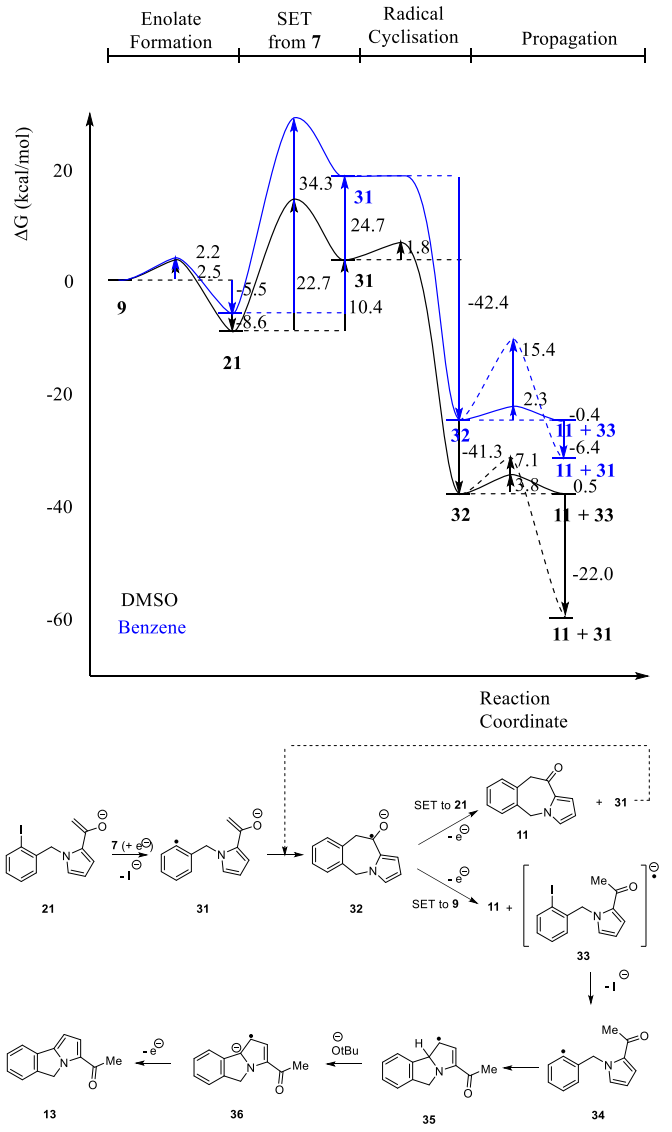
The energetic barriers, $\Delta G^*$, and the relative energies, $\Delta G_{rxn}$, for the SET to the anions **23**, **24**, **25**, derived from **15**, were determined and the reactivities were dramatically different when comparing the two solvents. In benzene, the major species present was determined to be **24**, however in DMSO the major species formed is **25**, *via* **24**. Therefore, in DMSO there are two possible electron-rich species present in the reaction mixture, **25** and **7**, which may both act as electron donors. The barriers for SET to **24** from both **7** and **25** were calculated in both benzene and DMSO. The barriers for the intermolecular SET are lower in both solvents when the electron donor is **25**, $\Delta G^*$ = 20.7 kcal/mol in DMSO, and $\Delta G^*$ = 18.4 kcal/mol in benzene. Interestingly in benzene the barrier for the SET from **25** would be accessible at RT, however it is important to note that the species **25** is not present in any significant quantity in the reaction mixture. Experimentally it was shown that the cyclisation of **15** proceeds in DMSO with similar efficiency in the absence of DKP, which suggests that the **25** is the electron donor in this reaction.[31]

An alternative process for the initiation pathway was an intramolecular SET (Scheme 4). The intramolecular SET for **21** was approximated through a number of approaches (Supporting Information, Section 1.5) which suggest that the intramolecular SET is energetically unfavourable. The HOMO and LUMO for **21** show a lack of orbital overlap in the optimized geometry of the molecule. This suggests that in the optimized geometry **21** has unfavourable energetics for intramolecular SET, and for the rest of the paper we will assume that the process occurs *via* intermolecular SET.

**The Cyclisation Mechanisms.**

*Cyclisation of 1-(1-(2-iodobenzyl)-1H-pyrrol-2-yl)ethan-1-one **9***

It has been determined that for these cyclisations, the solvent influences the equilibrium for the deprotonation of the substrates, as well as the energetic reaction profile for the SET step. The substrate **9** is predominantly present in the enolate anionic species **21** in the presence of KOtBu. SET from **7** (or from another molecule of **21**) to **21** leads to the formation of the aryl radical **31** upon the loss of iodide anion (Scheme 5). The radical intermediate **31** is capable of either undergoing an $S_{RN}1$ cyclisation, of the aryl radical onto the enolate anion, or an aryl-aryl bond formation, of the aryl radical onto the pyrrole ring. If the aryl radical **31** underwent an intramolecular cyclisation onto its enolate anion *via* an $S_{RN}1$ pathway, the ketyl radical **32** would be generated (Scheme 5). The $S_{RN}1$ cyclisation of intermediate **31**, in both benzene and DMSO, gave comparable Gibbs free energy profiles, with a barrierless cyclisation on the free energy surface and exergonic overall relative energies in the formation of **32**, $\Delta G_{rxn}$ = -42.4 and -41.3 kcal/mol respectively. The aryl-aryl bond formation of the radical **31** had a barrier of $\Delta G^*$ = 9.1 kcal/mol in DMSO and $\Delta G^*$ = 6.4 kcal/mol in benzene, which is greater than the barrierless $S_{RN}1$ cyclisation of the aryl radical onto the enolate anion (Supporting Information S2.1 and S2.2). Therefore in both solvents the cyclisation of **31** will proceed *via* the $S_{RN}1$ pathway to form **32**. The radical intermediate **32** will donate an electron, to a molecule of either **9** or **21**, to form the product **11** and in doing so propagate the radical chain reaction.



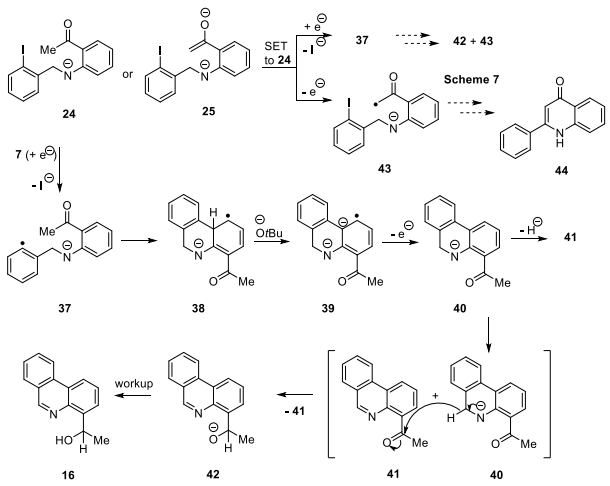

**Scheme 5**. The energy profile for the radical mechanism in the cyclisation of **9**

Due to the equilibrium for deprotonation of **9** it is most likely that the propagation will occur to **21**, since there is a greater proportion of this species present in the reaction mixture. This will lead to formation of **11** *via* the pathway described above. This was determined to be the most thermodynamically favoured propagation pathway. However an electron could be donated to **9** in the propagation step, and it was shown that this propagation step has a lower activation barrier and would be the kinetic propagation pathway. If the electron is donated to **9** the radical anion **33** is formed and aryl radical **34** forms on loss of iodide anion. Since there is no enolate anion in **34** the aryl radical will attack the pyrrole ring in the formation of an aryl-aryl bond, through the BHAS mechanism, to yield **13** upon deprotonation and propagation (Supporting Information, Scheme S2.1 and S2.2).

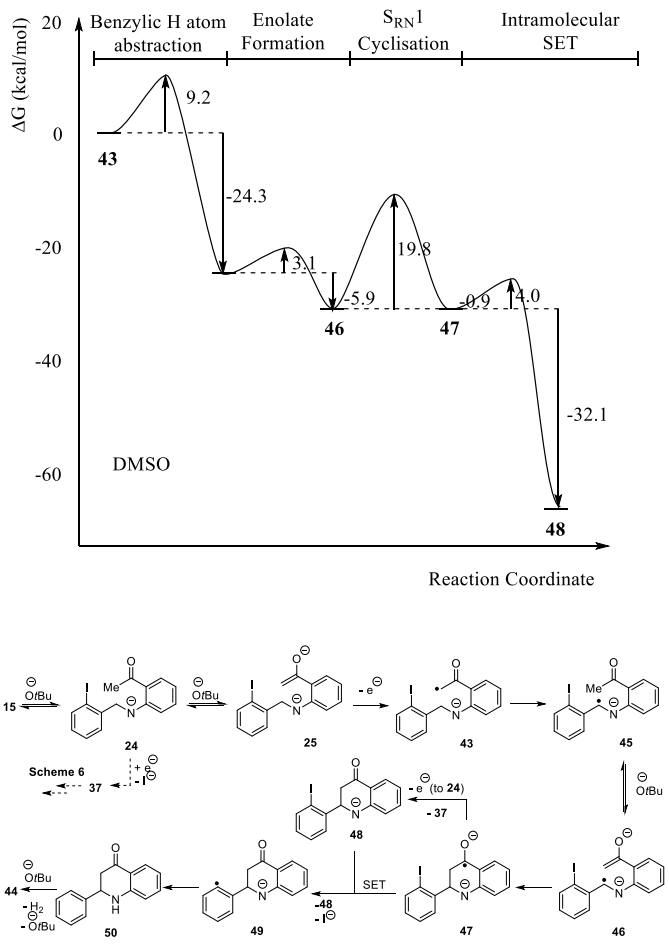
Therefore the major pathway will lead to product **11** and the product **13** will form as a minor product, only when propagation occurs to the neutral starting material **9**, which is only present in minor amounts in the basic reaction mixture. This revision of the previously proposed mechanism agrees with the experimental product selectivities observed.[31-32]

*Cyclisation of 1-(2-((2-iodobenzyl)amino)phenyl)ethan-1-one **15***

In DMSO the major deprotonated species derived from **15** will be **25**, whereas in benzene the major species is **24** (Table 1 and Table 2). Another difference between the two solvents is the energetic profile for the intermolecular SET initiation steps to these reactive species. Activation of **24** by SET, from **7** or **25**, forms the radical anion **37**, which will cyclise onto the aromatic system to yield **38** (Scheme 6). Upon deprotonation, **39** is achieved, which is capable of donating an electron to the reactive species, to propagate the cycle. The pathway for this aryl-aryl bond formation has been calculated in both benzene and DMSO, and it has been determined that both pathways have similar energy profiles for the cyclisation. Upon formation, **40** could undergo a hydride elimination to form **41**, which is driven by a gain in aromatic stabilization. If **41** is formation, **40** could undergo a hydride elimination to form **41**, which is driven by a gain in aromatic stabilization. If **41** is present in the reaction mixture it will form a complex with a molecule of **40**, possibly through π-stacking. Elimination of a hydride anion from **40** to **41** would yield a new molecule of **41** and the reduced product **16**, upon workup of intermediate **42** (Supporting Information, Scheme S3.1). In benzene the hydride transfer step from **40** to **41** is endergonic, $\Delta G_{rxn}$ = 5.0 kcal/mol, and it has an overall barrier of $\Delta G^*$ = 25.1 kcal/mol.[59] In DMSO the barrier for this reduction of **41** is similar to that in benzene, $\Delta G^*$ = 25.1 kcal/mol and $\Delta G_{rxn}$ = -1.0 kcal/mol. This barrier will be achievable at high temperatures however if the reaction is performed at room temperature, the reduction is unlikely to occur, which was observed experimentally.[31] Although the overall Gibbs free energy profile is similar in both the solvents, the relative energies are different, in DMSO the reduction is exergonic whereas in benzene the reduction is endergonic. Therefore in DMSO all of **41** is expected to be converted to **16**, whereas in benzene an incomplete conversion of **16** is predicted, which agrees with the experimental observations.[60] The major product present in the reaction mixture, with DMSO as a solvent, is **25**, which will undergo SET to **24**, in the initiation step, to form the radical anion **43** (Scheme 7).[61]




**Scheme 6**. Proposed mechanism in the cyclisation of the anionic species **24** and **25** arising from deprotonations of substrate **15**

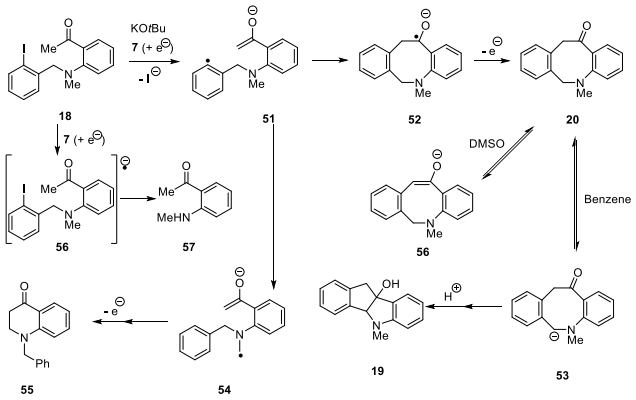



**Scheme 7.** The proposed mechanism in the cyclisation of **15**

The intermediate **43** could intramolecularly abstract a hydrogen atom from the benzylic position to yield the more stable radical anionic intermediate **45**. The energetics for this hydrogen atom abstraction were exergonic, $\Delta G^* = 9.2$ kcal/mol and $\Delta G_{rxn} = -24.3$ kcal/mol. In the basic reaction mixture an equilibrium will be established between **45** and the enolate anion **46**. In DMSO this equilibrium will largely favour the enolate anion $\Delta G^* = 3.1$ kcal/mol and $\Delta G_{rxn} = -5.9$ kcal/mol. If the enolate anion **46** forms, the benzylic radical will undergo an $S_{RN}1$ cyclisation onto the enolate anion to form **47**. This pathway in DMSO has a barrier for cyclisation of $\Delta G^* = 19.8$ kcal/mol and a relative energy of $\Delta G_{rxn} = -0.9$ kcal/mol. This means that in DMSO the cyclized product **47** is going to be present in high proportions, and will therefore proceed along the reaction pathway to form the **49** upon SET. It was proposed that in DMSO **47** could undergo an intramolecular SET in the formation of the intermediate **49** (Supporting Information, Section 3.3), however it was determined that intermolecular SET was the most favoured energetically. SET from **47** (to **24**) will yield an anionic intermediate **48**. This intermediate can receive an electron (from **47**) into the C-I $\sigma^*$ orbital, to cleave the C-I bond and form an aryl radical intermediate **49**. The aryl radical within **49** is very reactive and will be quenched in the reaction mixture to form **50**. Molecule **50** can form **44** in two steps (i) a butoxide anion will form the enolate anion of **50** and (ii) this enolate anion will undergo a hydride elimination to a molecule of butanol, to form **44** and hydrogen, and regenerate the butoxide anion (Supporting Information, Scheme S3.5). The energetic profile for the hydride elimination in the formation of **44** from **50** is exergonic, $\Delta G_{rxn} = -7.0$ kcal/mol, with an barrier of $\Delta G^* = 21.6$ kcal/mol. This energetic barrier is the RDS in the reaction pathway and it suggests that lowering the reaction temperature may lead to the isolation of the intermediate **50**, which was shown experimentally.[6] The influence of solvent in the cyclisation of **15** is to control which reactive species (**24** and **25**) is present in the reaction mixture, and because these reactive intermediates undergo different pathways the selectivity of the reaction can be controlled by changing the solvents. In DMSO the reaction will selectively form **44** from the intermediate **25**, however in benzene the reaction will selectively favour the formation of **41**. It has also been shown that the temperature can be altered to dictate product formation, at low temperatures **41** will be the major product formed in benzene, however increasing that temperature will lead to the formation of **16**. Similarly in DMSO, lowering the reaction temperature could reduce the formation of **44** and the intermediate **50** can be isolated.

*Cyclisation of 1-(2-((2-iodobenzyl)(methyl)amino)phenyl)ethan-1-one **18***

The cyclisation of **18** involves the SET initiation to the enolate anion **22**, which could occur at RT in DMSO, however higher temperatures should be used for the reaction in benzene. The solvent influence on the SET to **18** shows similar trends as **9**. Upon SET, the aryl radical intermediate **51** could undergo either an $S_{RN}1$ cyclisation onto the enolate anion to form **52**, or H atom abstraction from the methyl group, to form radical **54** (Scheme 8) (Supporting Information, Scheme S4.1). The $S_{RN}1$ cyclisation of **51** onto the enolate anion is calculated to be the most favoured pathway in both benzene and DMSO. Cyclisation of **51** ultimately forms **20** which in the presence of a base **20** could be deprotonated either to form the enolate anion **56** or to form the benzylic anion **53**. In both solvents the favoured deprotonation is the enolate formation to form **56**. In DMSO the benzylic deprotonation to form **52** was endergonic, $\Delta G_{rxn} = 4.9$ kcal/mol, however in benzene the deprotonation of the benzylic position to form **52** has similar energetics to this enolate anion formation (Supporting Information, Scheme S4.1). Therefore in benzene the deprotonation equilibrium would form intermediate **52** and this benzylic attack can ionically attack the carbonyl group to form **19** upon workup. Therefore if the reaction is performed in DMSO, the product **20** is formed through this reaction pathway and the reaction can be performed at RT, and in benzene the product formed will be **19**, however because the reaction is performed in benzene the reaction must be performed at high temperatures to overcome the energetic barrier for the SET initiation step.




**Scheme 8.** The proposed mechanism in the cyclisation of **18**

In both solvents the minor pathway of **51** is the hydrogen atom abstraction to form **54** and ultimately **55** (Supporting Information, Scheme S4.2). In benzene, **51** will cyclise to form **52** with a barrierless transition, whereas in DMSO the transition has a barrier of $\Delta G^* = 2.7$ kcal/mol. Therefore in benzene it is predicted that the $S_{RN}1$ pathway will be the major pathway whereas in DMSO there will be less selectivity for this $S_{RN}1$ cyclisation, and this is seen experimentally.[6]

An interesting observation during this study is that in the propagation step, SET from **52** can occur either to the enolate anion **22** or to the neutral species **18** (Supporting Information, Scheme S4.3). It was found that in both solvents, the lowest barrier is SET to the neutral species, not the enolate anionic species. If this occurs then the radical anion **56** forms, which can undergo fragmentation to form **57** upon workup. However, this pathway will be a minor pathway due to the low population of **18** that will be present in the reaction mixture.

## Conclusions

This paper has thoroughly investigated the mechanistic pathways through which various C-C bonds are formed under ground-state thermal activation. The experimental results have been shown to support the proposed pathways and these mechanisms are different from those previously reported, and the rate determining steps for the radical steps in these mechanisms is shown to be the initiation SET step.[31-32] With increased knowledge of these pathways, we could fine tune the reaction conditions to lead to efficient C-C bond formations.

Solvent was also shown to affect various reaction pathways because of its more commonly accepted role in the stabilization of intermediates in ionic pathways. Changing the polarity of the solvent was a useful mechanism to influence the product outcomes of radical pathways. The deprotonation energetics were largely influenced by the solvent and this resulted in different reactive species being present prior to the SET step. The largest influence of the choice of solvent on these reaction pathways is on the SET steps, such as the initiation and the propagation steps. The SET step is often the rate determining step in both solvents, and so using DMSO as the solvent instead of benzene allowed milder reaction conditions to be employed for efficient cyclisation. However in some circumstances the rate determining step in DMSO was not the SET and so using milder reaction conditions led to formation of new products, which are intermediates in the reaction pathway. In the cyclisation of substrate **15** the choice of solvent influenced the stability of radical intermediates within the cyclisation pathway and thus changed the product outcomes of the cyclisation.

The species that could act as the electron donor in the SET step was also changed when changing solvents from benzene to DMSO. The additive DKP was not required when DMSO was the solvent since the enolate anions of the species themselves were capable of performing the SET step.

## Acknowledgements

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## Notes and references

1. C. Reichardt, *Pure Appl. Chem.* 1982, **54**, 1867.
2. J. B. F. N. Engberts, *Angew. Chem. Int. Ed.* 2004, **43**, 2744.
3. C. Reichardt; T. Welton, Solvent Effects on the Position of Homogeneous Chemical Equilibria. In *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: 2010; pp 107-163.
4. C. Reichardt; T. Welton, Solvent Effects on the Absorption Spectra of Organic Compounds. In *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: 2010; pp 359-424.
5. C. Reichardt; T. Welton, Solvent Effects on the Rates of Homogeneous Chemical Reactions. In *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: 2010; pp 165-357.
6. H. Miya; Y. Takemoto, *Universal Organic Chemistry* 2014, **2**.
7. J. C. Lo; J. Gui; Y. Yabe; C.-M. Pan; P. S. Baran, *Nature* 2014, **516**, 343.
8. S. L. Castle, *Nature* 2014, **516**, 332.
9. G. Bar; A. F. Parsons, *Chem. Soc. Rev.* 2003, **32**, 251.
10. G. J. Rowlands, *Tetrahedron* 2009, **65**, 8603.
11. G. J. Rowlands, *Tetrahedron* 2010, **66**, 1593.
12. M. Yan; J. C. Lo; J. T. Edwards; P. S. Baran, *J. Am. Chem. Soc.* 2016, **138**, 12692.
13. S. Yanagisawa; K. Ueda; T. Taniguchi; K. Itami, *Org. Lett.* 2008, **10**, 4673.
14. A. Studer; D. P. Curran, *Angew. Chem. Int. Ed.* 2011, **50**, 5018.
15. S. Zhou; G. M. Anderson; B. Mondal; E. Doni; V. Ironmonger; M. Kranz; T. Tuttle; J. A. Murphy, *Chem. Sci.* 2014, **5**, 476.
16. S. Zhou; E. Doni; G. M. Anderson; R. G. Kane; S. W. MacDougall; V. M. Ironmonger; T. Tuttle; J. A. Murphy, *J. Am. Chem. Soc.* 2014, **136**, 17818.
17. E. Shirakawa; K.-i. Itoh; T. Higashino; T. Hayashi, *J. Am. Chem. Soc.* 2010, **132**, 15537.
18. W. Liu; H. Cao; H. Zhang; H. Zhang; K. H. Chung; C. He; H. Wang; F. Y. Kwong; A. Lei, *J. Am. Chem. Soc.* 2010, **132**, 16737.
19. C.-L. Sun; H. Li; D.-G. Yu; M. Yu; X. Zhou; X.-Y. Lu; K. Huang; S.-F. Zheng; B.-J. Li; Z.-J. Shi, *Nat Chem* 2010, **2**, 1044.
20. C.-L. Sun; Y.-F. Gu; B. Wang; Z.-J. Shi, *Chem. Eur. J.* 2011, **17**, 10844.
21. E. Shirakawa; X. Zhang; T. Hayashi, *Angew. Chem. Int. Ed.* 2011, **50**, 4671.
22. E. Z. Doni, S.; Murphy, J.A., *Molecules* 2015, **20**, 1755.
23. M. Rueping; M. Leiendecker; A. Das; T. Poisson; L. Bui, *Chem. Commun.* 2011, **47**, 10629.
24. H. Zhang; R. Shi; A. Ding; L. Lu; B. Chen; A. Lei, *Angew. Chem. Int. Ed.* 2012, **51**, 12542.
25. J. F. Bunnett; R. G. Scamehorn; R. P. Traber, *J. Org. Chem.* 1976, **41**, 3677.
26. R. G. Scamehorn; J. F. Bunnett, *J. Org. Chem.* 1977, **42**, 1449.
27. M. Pichette Drapeau; I. Fabre; L. Grimaud; I. Ciofini; T. Ollevier; M. Taillefer, *Angew. Chem. Int. Ed.* 2015, 10587.
28. R. A. Rossi; J. F. Bunnett, *J. Org. Chem.* 1973, **38**, 1407.
29. J. F. Bunnett; J. K. Kim, *J. Am. Chem. Soc.* 1970, **92**, 7463.
30. R. G. Scamehorn; J. M. Hardacre; J. M. Lukanich; L. R. Sharpe, *J. Org. Chem.* 1984, **49**, 4881.
31. K. J. Emery; T. Tuttle; A. R. Kennedy; J. A. Murphy, *Tetrahedron* 2016, **72**, 7875.
32. J. F. Guastavino; R. A. Rossi, *J. Org. Chem.* 2012, **77**, 460.
33. Y. Zhao; D. G. Truhlar, *Acc. Chem. Res.* 2008, **41**, 157.
34. Y. Zhao; D. G. Truhlar, *J. Chem. Phys.* 2006, **125**, 194101.
35. R. Krishnan; J. S. Binkley; R. Seeger; J. A. Pople, *J. Chem. Phys.* 1980, **72**, 650.
36. M. J. Frisch; J. A. Pople; J. S. Binkley, *J. Chem. Phys.* 1984, **80**, 3265.
37. A. D. McLean; G. S. Chandler, *J. Chem. Phys.* 1980, **72**, 5639.
38. J.-P. Blaudeau; M. P. McGrath; L. A. Curtiss; L. Radom, *J. Chem. Phys.* 1997, **107**, 5016.
39. T. Clark; J. Chandrasekhar; G. W. Spitznagel; P. V. R. Schleyer, *J. Comput. Chem.* 1983, **4**, 294.
40. A. Bergner; M. Dolg; W. Küchle; H. Stoll; H. Preuß, *Mol. Phys.* 1993, **80**, 1431.
41. M. Cossi; N. Rega; G. Scalmani; V. Barone, *J. Comput. Chem.* 2003, **24**, 669.
42. V. Barone; M. Cossi, *J. Phys. Chem. A* 1998, **102**, 1995.
43. M. J. Frisch; G. W. Trucks; H. B. Schlegel; G. E. Scuseria; M. A. Robb; J. R. Cheeseman; G. Scalmani; V. Barone; B. Mennucci; G. A. Petersson; H. Nakatsuji; M. Caricato; X. Li; H. P. Hratchian; A. F. Izmaylov; J. Bloino; G. Zheng; J. L. Sonnenberg; M. Hada; M. Ehara; K. Toyota; R. Fukuda; J. Hasegawa; M. Ishida; T. Nakajima; Y. Honda; O. Kitao; H. Nakai; T. Vreven; J. A. Montgomery Jr.; J. E. Peralta; F. Ogliaro; M. J. Bearpark; J. Heyd; E. N. Brothers; K. N. Kudin; V. N.

Staroverov; R. Kobayashi; J. Normand; K. Raghavachari; A. P. Rendell; J. C. Burant; S. S. Iyengar; J. Tomasi; M. Cossi; N. Rega; N. J. Millam; M. Klene; J. E. Knox; J. B. Cross; V. Bakken; C. Adamo; J. Jaramillo; R. Gomperts; R. E. Stratmann; O. Yazyev; A. J. Austin; R. Cammi; C. Pomelli; J. W. Ochterski; R. L. Martin; K. Morokuma; V. G. Zakrzewski; G. A. Voth; P. Salvador; J. J. Dannenberg; S. Dapprich; A. D. Daniels; Ö. Farkas; J. B. Foresman; J. V. Ortiz; J. Cioslowski; D. J. Fox *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, USA, 2009.

44. G. B. Bajracharya; O. Daugulis, *Org. Lett.* 2008, **10**, 4625.

45. Substrate **9** undergoes cyclisation to **11** and **13** in the presence of KOtBu, $FeCl_2$ and pinacolone. It can also undergo cyclisation under photoactivation in presence of KOtBu.

46. **10** was shown to cyclise in the presence of additive DKP **6** (31% benzene at 120 °C; 62% DMSO at 120 °C; 54% DMSO at RT).

47. C. Costentin; M. Robert; J.-M. Savéant, *J. Am. Chem. Soc.* 2004, **126**, 16834.

48. C. Costentin; M. Robert; J.-M. Savéant, *J. Am. Chem. Soc.* 2004, **126**, 16051.

49. S. Antonello; F. Maran, *J. Am. Chem. Soc.* 1997, **119**, 12595.

50. It must be noted that it has been proposed within the literature that the dimsyl anion is capable of donating an electron to initiate the transition metal free reaction conditions (reference 51 - 53). The KOtBu deprotonation of DMSO was determined to be endogonic, $\Delta G^*$ = 5.6 kcal/mol and $\Delta G_{rxn}$ = 5.4 kcal/mol, and the SET from the dimsyl anion to **21** was determined to be $\Delta G^*$ = 29.5 kcal/mol and $\Delta G_{rxn}$ = 20.8 kcal/mol. This gave an overall value of $\Delta G^*$ = 34.9 kcal/mol and $\Delta G_{rxn}$ = 26.2 kcal/mol for SET from a dimsyl anion. This is less favourable than the SET from **7** or **21** and therefore we conclude the dimsyl anion is not initiating the reaction in this situation.

51. S. Rajan; K. Muralimohan, *Tetrahedron Lett.* 1978, **19**, 483.

52. R. A. Alonso; R. A. Rossi, *Tetrahedron Lett.* 1985, **26**, 5763.

53. M.-X. Zhang; X.-H. Hu; Y.-H. Xu; T.-P. Loh, *Asian J. Org. Chem.* 2015, **4**, 1047.

54. R. A. Marcus, *J. Chem. Phys.* 1965, **43**, 679.

55. Experimentally at 120 °C in benzene without the **7** only 23% of **11** was observed in benzene. Since none of **13** was observed we can propose that the small amount of **11** formed through the benzyne pathway.

56. At room temperature in DMSO the reaction efficiently yielded product **11** and **13**. In benzene however only traces of **11** were observed, and starting material was returned.

57. Murphy *et al.* (reference 31) reported that when the reaction was performed in benzene in the absence of the DKP additive **6**, the starting material, **9**, was recovered with 73%.

58. H. Heitele, *Angew. Chem. Int. Ed.* 1993, **32**, 359.

59. When the reaction was performed in DMSO at room temperature only the product **16** was observed. No **42** was observed.

60. In DMSO the reduced product **42** was isolated at 120 °C, whereas in benzene both **42** and **16** were isolated. At room temperature the reduction of **16** is not observed in DMSO and only **16** was isolated.

61. Experimentally the substrate **15** will undergo cyclisation in the absence of the DKP additive in both benzene and DMSO, with similar yields to when DKP additive was used (reference 31). This suggests that a deprotonated species of **15** is capable of acting as the electron donor.

# Effect of solvent on radical cyclisation pathways: $S_{RN}1$ vs. aryl-aryl bond forming mechanisms

Katie J. Emery, John A. Murphy, and Tell Tuttle

## SUPPORTING INFORMATION

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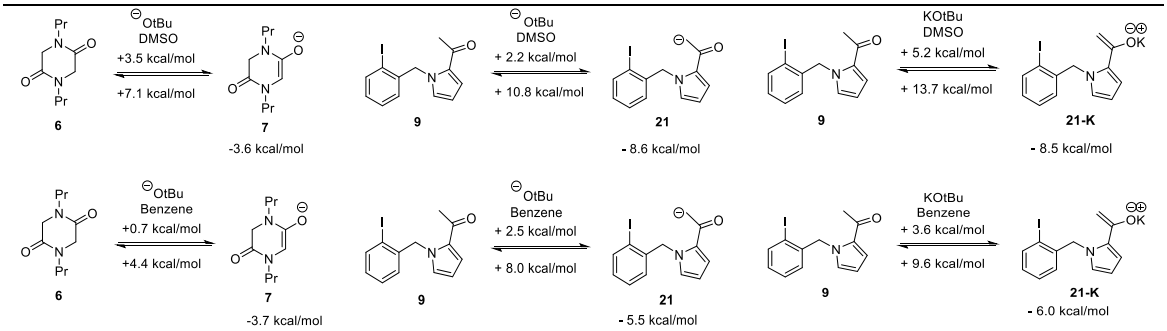
# 1. Initiation Calculations

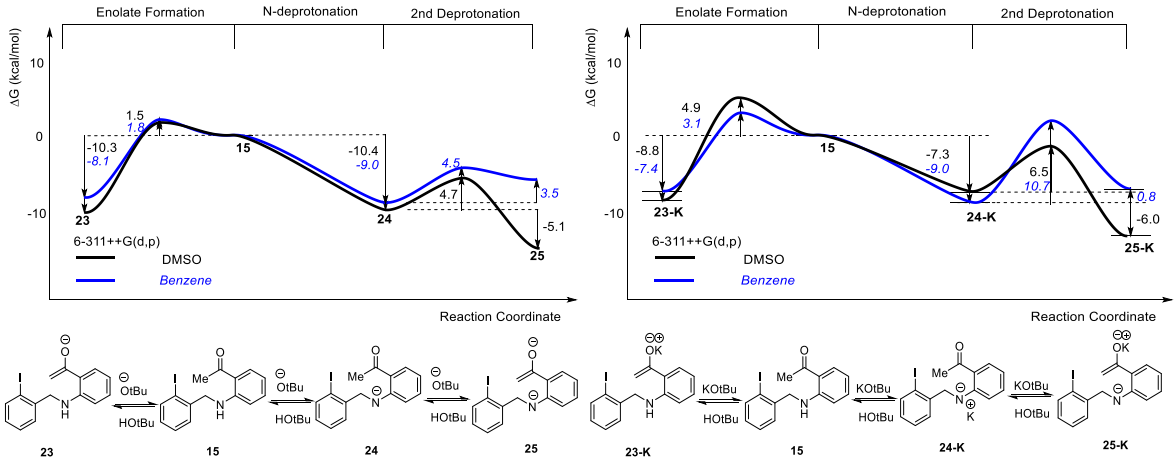
## 1.1 Enolate Formation

Table S1.1. The deprotonation energetics for DKP and substrate **9** in both DMSO and benzene



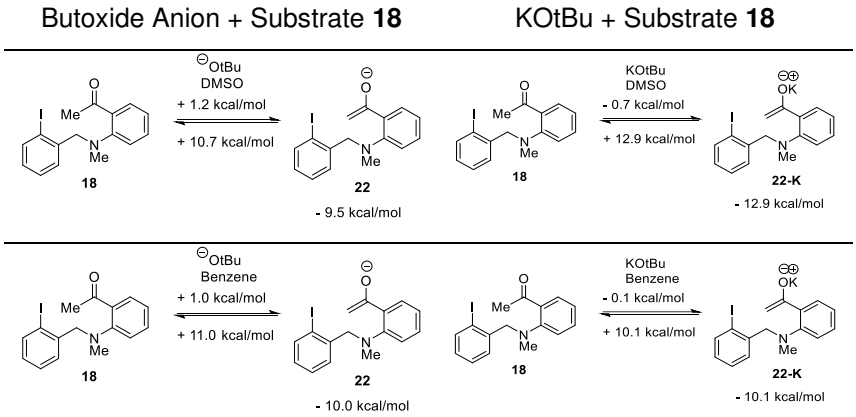

In the basic reaction mixture, the diketopiperazine (DKP) additive **6** will exist predominantly as the enolate anion **7**. The substrate **9** will be in equilibrium with its enolate anion **21** in the presence of base, and the enolate anion **21** will be the major species in both benzene and DMSO. The energetics for the deprotonation of **9** using the tertiary butyl anion or the KOtBu as the base are similar.

Scheme S1.1. The deprotonation energetics for substrate **15** with either a molecule of tertiary butoxide anion or with KOtBu in both DMSO and benzene




In the basic reaction mixture the substrate **15** will be in equilibrium with its various possible deprotonation states. In benzene the most stable species will be **24** and in DMSO the most stable species present will be **25**.

Table S1.2. The deprotonation energetics for substrate **18** with either a molecule of tertiary butoxide anion or with KOtBu in both DMSO and benzene

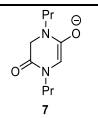
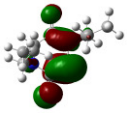
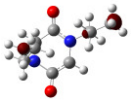
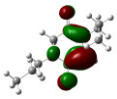
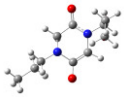
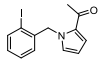
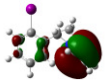
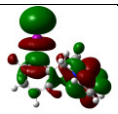
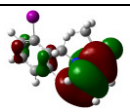
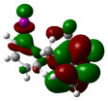
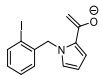
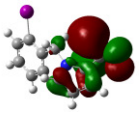
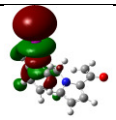
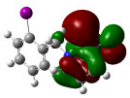
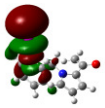
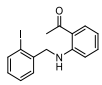
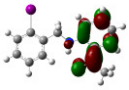
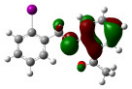
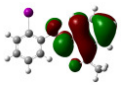
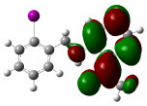
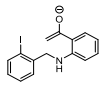
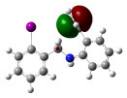
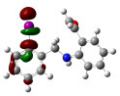
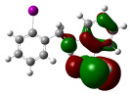
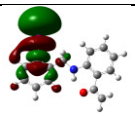
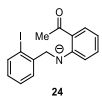
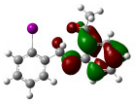
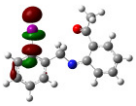
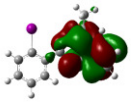
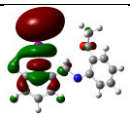
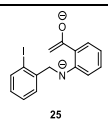
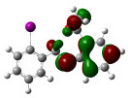
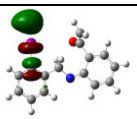
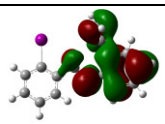
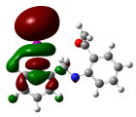
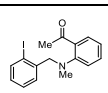
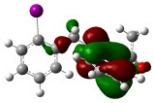
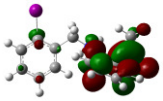
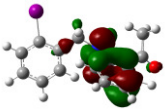
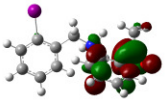
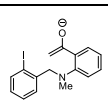
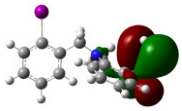
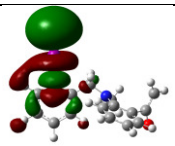
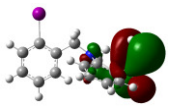
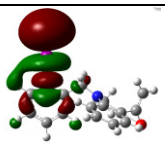
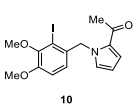
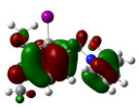
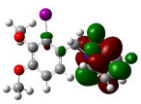
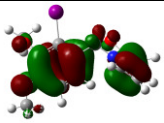
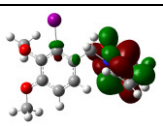



In the basic reaction mixture the substrate **18** will be in equilibrium with its enolate anion **22**. The equilibrium will strongly reside towards the enolate anion **22** in both the solvents.

In the modelling of the reactions from this point throughout the paper, the calculations for the deprotonations will use the butoxide anion for the deprotonations for computational cost and because the results are similar for the equilibrium.

## 1.2 HOMO-LUMO Diagrams

Table S1.3. The HOMO and LUMO diagrams of reactive species

| | Benzene as Solvent | | DMSO as Solvent | |
|---|---|---|---|---|
| | HOMO | LUMO | HOMO | LUMO |
|  7 |  |  |  |  |
|  9 |  |  |  |  |
|  21 |  |  |  |  |
|  15 |  |  |  |  |
|  23 |  |  |  |  |
|  24 |  |  |  |  |
|  25 |  |  * |  |  |
|  18 |  |  |  |  |
|  22 |  |  |  |  |
|  10 |  |  |  |  |

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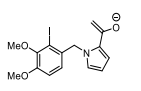
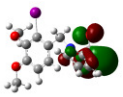
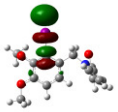
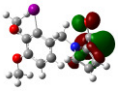
|  S1 |  |  |  |  |

* LUMO+2 orbital

Table S1.4. Spin density diagrams of the substrates after accepting an electron by SET

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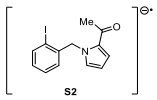
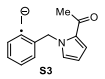
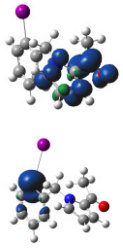
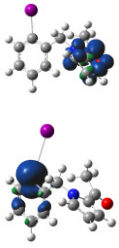
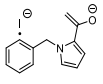
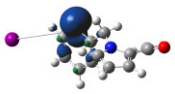
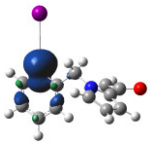
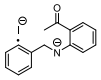
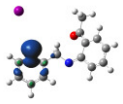
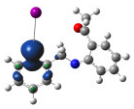
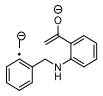
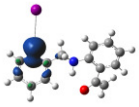
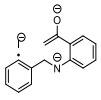
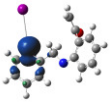
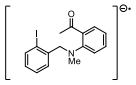
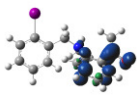
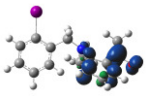
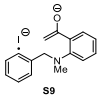
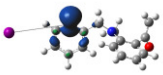
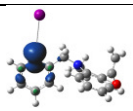
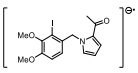
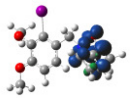
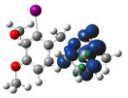
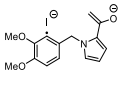
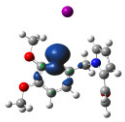
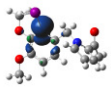
|---|---|---|---|---|---|
|  S2  S3 |  |  |  S4 |  |  |
|  S5 |  |  |  S6 |  |  |
|  S7 | |  |  S8 |  |  |
|  S9 |  |  |  S10 |  |  |
|  S11 |  |  | | | |

Table S1.5. Spin density diagrams of the substrates after donating a single electron

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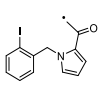
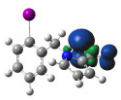
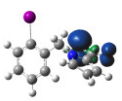
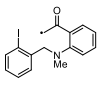
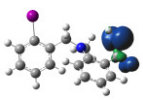
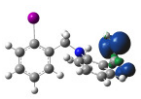
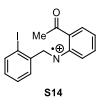
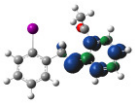
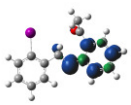
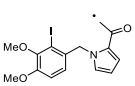
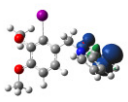
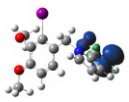
|  S12 |  |  |  S13 |  |  |
|  S14 |  |  |  S15 |  |  |

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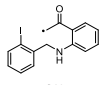
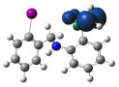
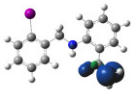
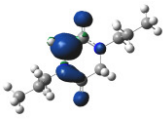
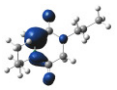
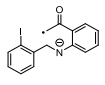
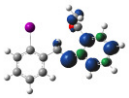
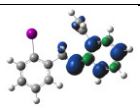
|  S16 |  |  |  8 |  |  |
|  43 |  |  | | | |

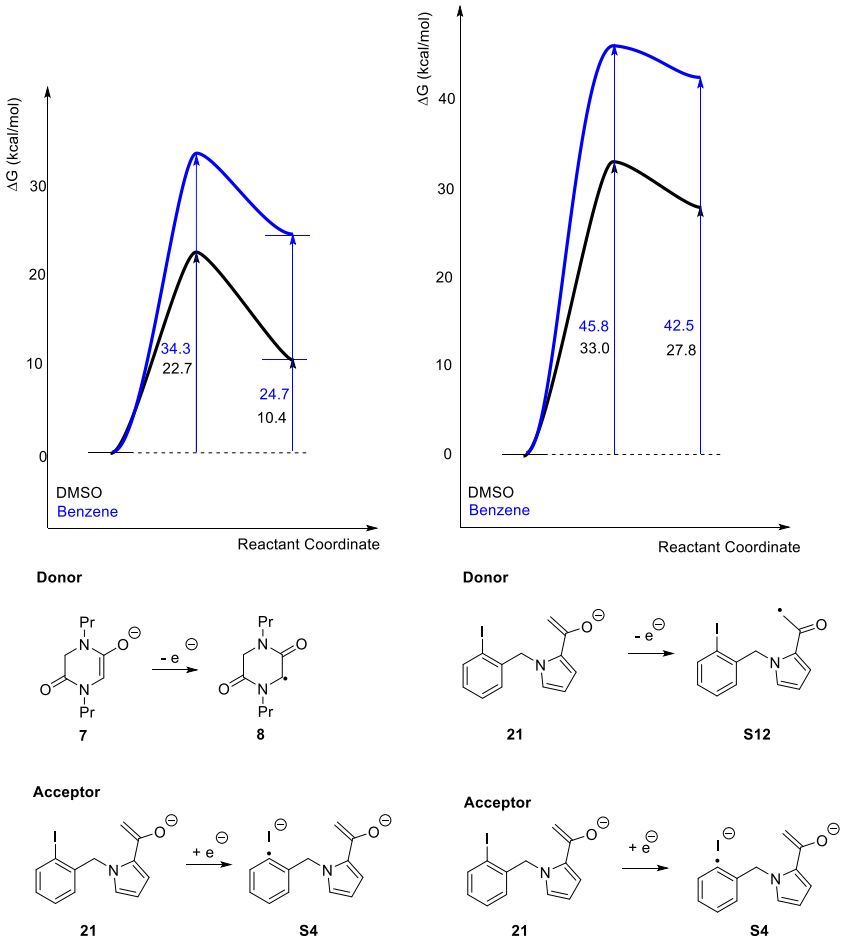
## 1.3 Energetics of SET – Marcus Hush Theory

Table S1.6. The energetics for the SET initiation to either the neutral or anionic species of substrates **9**, **10**, **15** or **18**, from either the in situ electron donor **7** or the respective anionic species of the substrates **21**, **23**, **24**, **25**, **22** or **S1** in both benzene and DMSO

| Electron Acceptor | Electron Donor | Benzene $\Delta G^*$ | Benzene $\Delta G_{rxn}$ | DMSO $\Delta G^*$ | DMSO $\Delta G_{rxn}$ |
|---|---|---|---|---|---|
| **9** | **7** | 31.9 | 30.7 | 36.0 | 32.8 |
| **9** [a.] | **7** | 18.1 | 5.7 | 20.1 | 8.9 |
| **21** | **7** | 34.3 | 24.7 | 22.7 | 10.4 |
| **9** | **21** | 69.2 | 48.5 | 74.1 | 50.2 |
| **9** [a.] | **21** | 27.9 | 23.5 | 30.5 | 26.3 |
| **21** | **21** | 45.8 | 42.5 | 33.0 | 27.8 |
| **23** | **7** | 30.9 | 21.9 | 21.3 | 8.4 |
| **24** | **7** | 38.7 | 34.3 | 23.3 | 11.4 |
| **25** | **7** | -- | -- | 22.3 | 13.1 |
| **23** | **23** | 42.8 | 39.6 | 31.2 | 25.3 |
| **23** | **24** | 45.4 | 43.4 | 30.6 | 24.5 |
| **23** | **25** | 13.3 | -6.1 | 18.7 | 7.1 |
| **24** | **25** | 18.4 | 6.2 | 20.7 | 10.1 |
| **25** | **25** | -- | -- | 19.8 | 11.8 |
| **18** [b.] | **7** | 27.8 | 27.6 | 32.3 | 31.1 |
| **22** | **7** | 31.7 | 23.1 | 22.3 | 10.8 |
| **22** | **22** | 43.3 | 40.1 | 31.0 | 26.5 |
| **10** [b.] | **7** | 34.9 | 31.7 | 37.5 | 34.4 |
| **S1** | **7** | 33.9 | 25.3 | 22.6 | 9.8 |
| **S1** | **S1** | 45.0 | 41.6 | 32.0 | 25.6 |

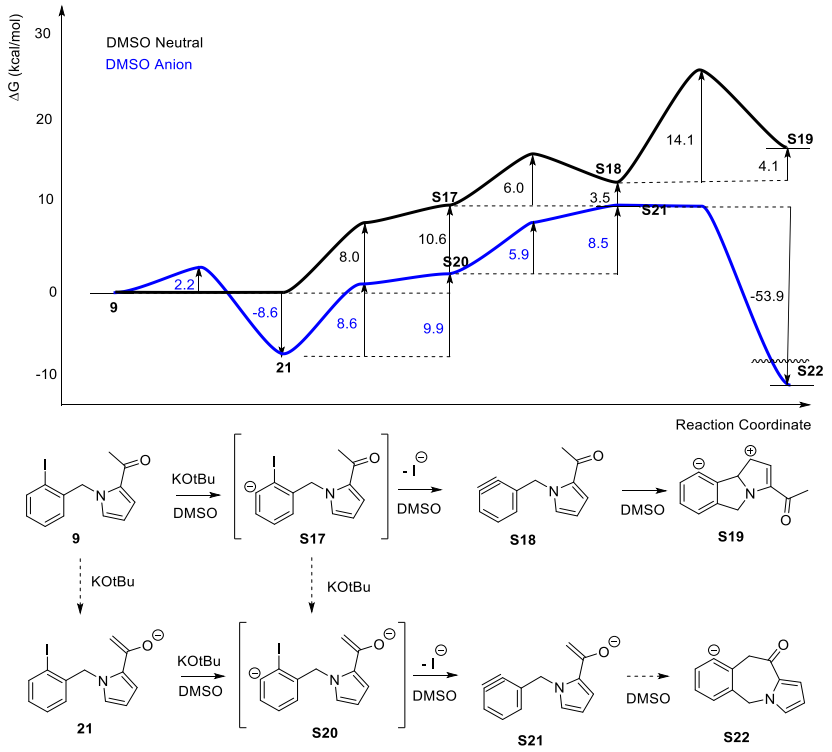
[a.] Encouraged C-I dissociation. [b.] Did not give C-I dissociation.

Scheme S1.2. The energetics for the possible intermolecular SET between **7** or **21** to **9** in both DMSO and benzene.



# 1.4 Benzyne Pathway

Scheme S1.3. The energetics for possible benzyne formation in DMSO from **9** and **21**

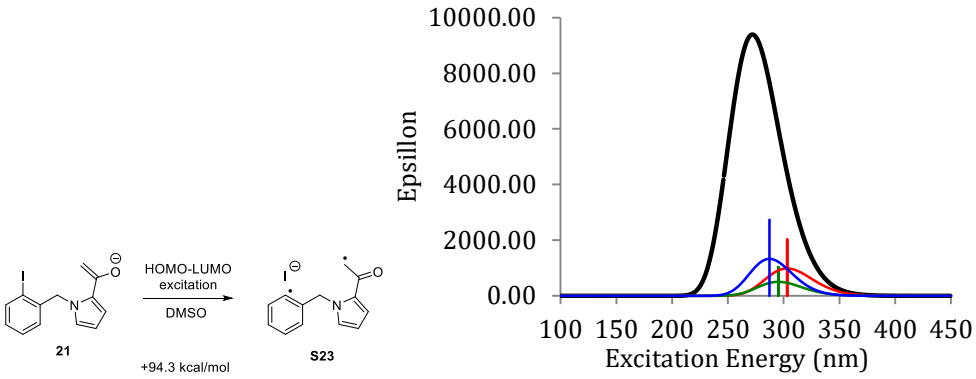



The benzyne formation is accessible at RT in DMSO however it is very endergonic. The formation of the neutral benzyne **S18** is $\Delta G_{rxn}$ = 14.1 kcal/mol, and to form **S21** the reaction is endergonic by $\Delta G_{rxn}$ = 18.4 kcal/mol. The cyclisation to form **S19** has an overall $\Delta G^*$ = 28.2 kcal/mol and $\Delta G_{rxn}$ = 18.2 kcal/mol. This is very unfavourable and the product **13** would not form if the reaction proceeded through the benzyne mechanism. The cyclisation of **S21** to **S22** is barrierless and very exothermic, suggesting that if any benzyne forms, then the cyclisation to form **11** will occur. Therefore it is possible that partial amount of the formation of **11** may occur via this pathway.

# 1.5 Intramolecular Analysis of 9

## 1.5.1 TD DFT

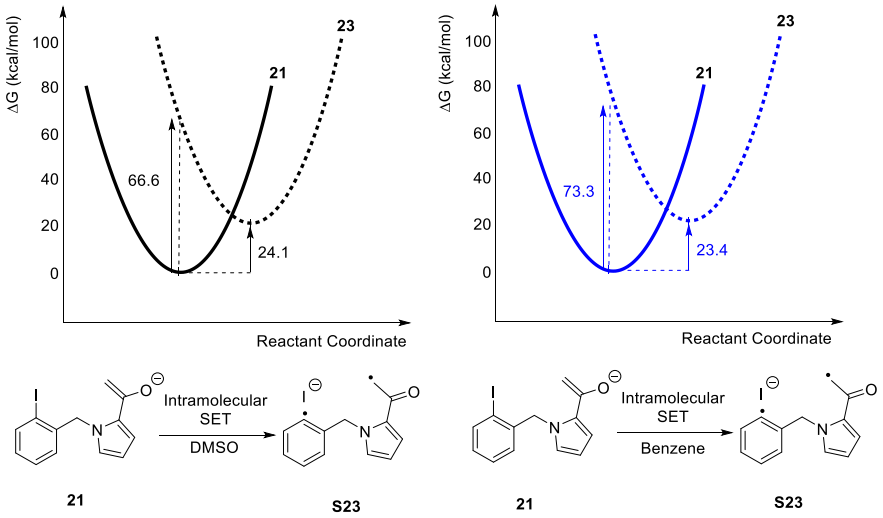
Scheme S1.4: The TDDFT calculations were performed on **21**. The Gaussian curve was generated using the default Gaussian parameters. Black lines = Overall predicted UV-Vis trace. Red Blue and Green vertical transitions correspond to HOMO – LUMO excitations.




The TDDFT results suggests that the intramolecular SET is not possible for **21** in DMSO.

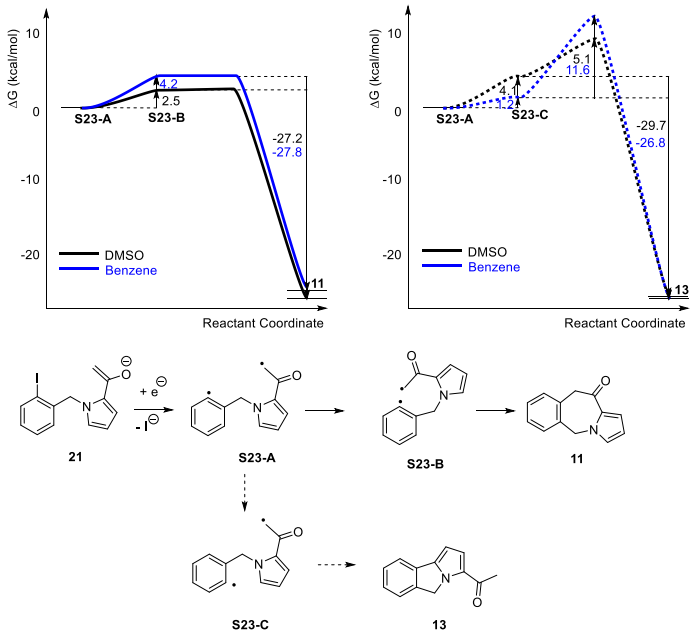
## 1.5.2 Franck-Condon

Scheme S1.5. The energetics intramolecular SET for **21** in both DMSO and Benzene, calculated using the Frank-Condon principle



The Frank-Condon principle states that the electron transfer step occurs first prior to reorganization of substrates and solvent. Therefore the energetics for intramolecular SET were determined by optimizing the anionic species, and performing a single point energy calculation, on this optimized geometry, using the triplet anion charge and multiplicity. It showed that the intramolecular SET of **21** is not likely to occur in either of the two solvents.

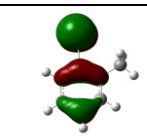
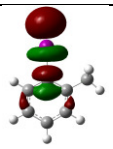
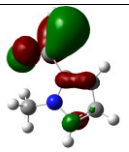
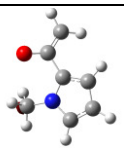
Scheme S1.6. The energetics radical recombination




The results suggest that if the molecule **21** was able to undergo an intramolecular SET initiation pathway then the resulting diradical **S23-A** would easily cyclise to form either **11** or **13** through radical recombination.

### 1.5.3 SET between the isolated HOMO-LUMO fragments of 21

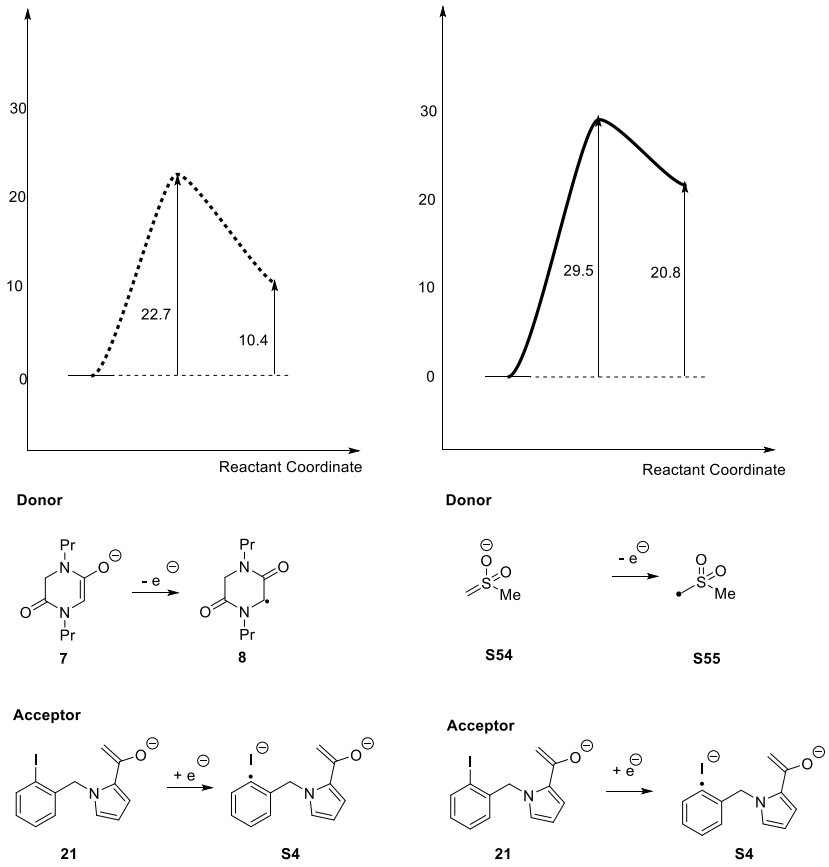
Scheme S1.7. The energetics for an intermolecular SET between the isolated HOMO and LUMO fragments of substrate **21**. The table displays the HOMO/LUMO of the fragments


| | HOMO | LUMO |
|---|---|---|
| S24 |  |  |
| S25 |  |  |

The results for the SET between the two fragments yields similar results as the intermolecular SET between two molecules of **21**. The analysis of the HOMO and LUMO for the fragments **S24** and **S25** and for the molecules of **21** are very similar, emphasising that the HOMO and LUMO orbitals of **21** do not overlap in the optimized geometry. This lack of orbital overlap between the HOMO and LUMO of **21** provides a possible explanation for the high energetics calculated for intramolecular SET.

# 1.6 Possible SET from the dimsyl anion

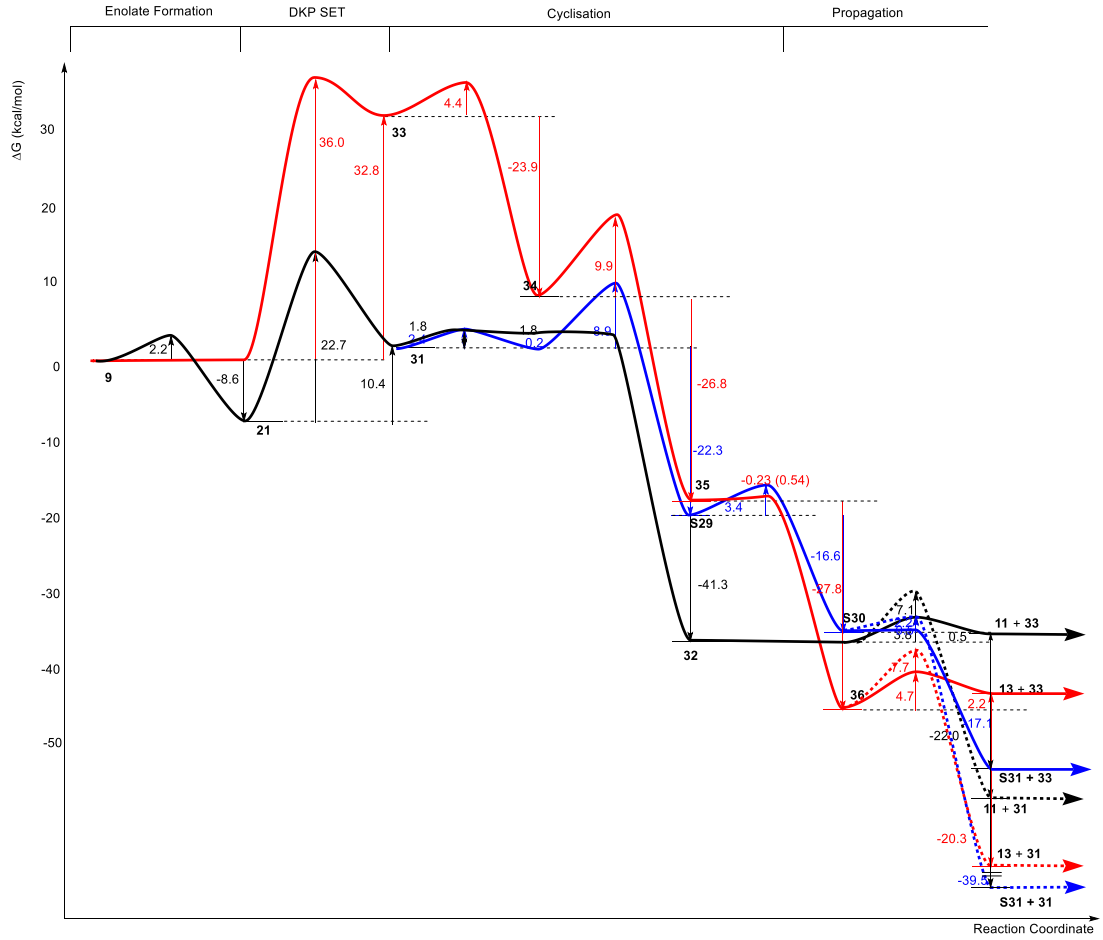
Scheme S1.8. The energetics for an SET from either **7** or a dimsyl anion **S54**, to the enolate anion **21** od substrate **9**



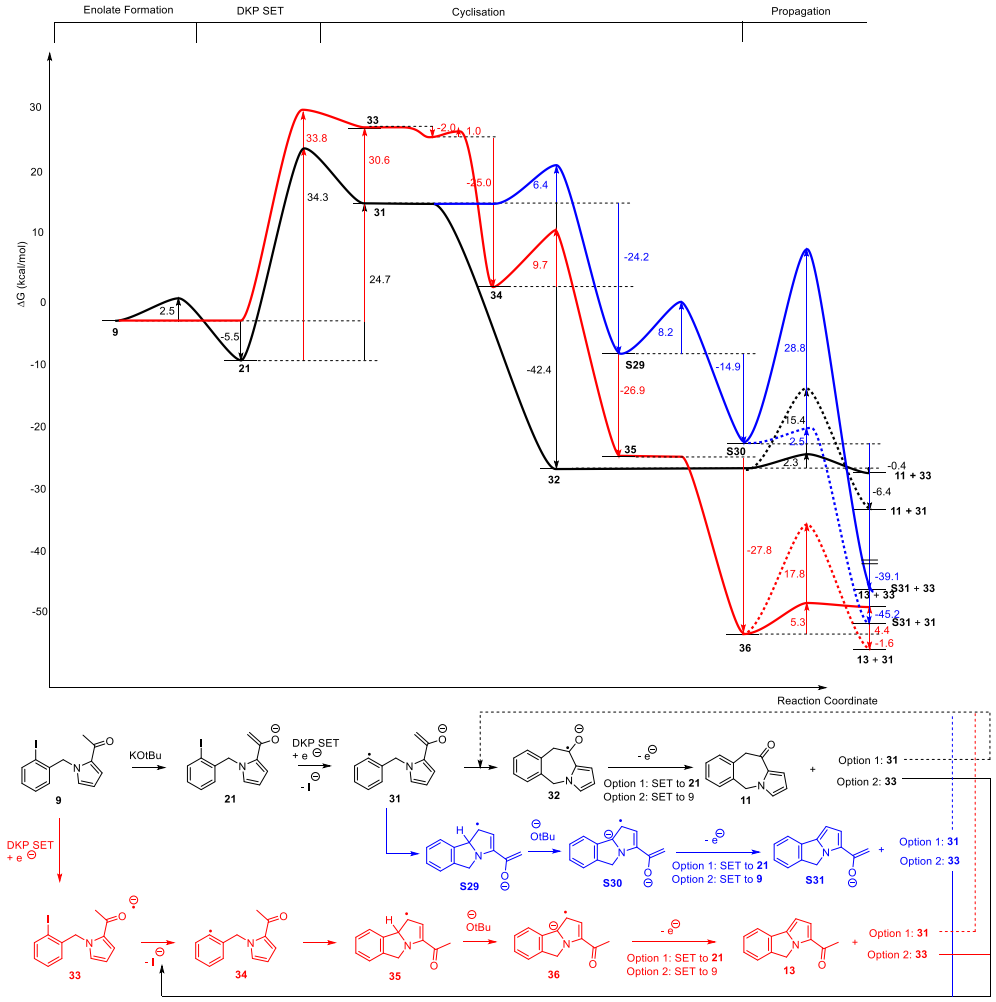

Within the literature it was proposed that the dimsyl anion (formed from the deprotonation of DMSO) was able to donate a single electron to the iodobenzene to form an aryl radical. Therefore the energetics for the SET from the dimsyl anion to the substrate **21** was calculated. This $\Delta G^*$ was compared with the barrier for the SET from the enolate anion of DKP **7**. It was shown that the dimsyl anion could donate an electron to **21** at elevated temperatures in DMSO, however the favoured pathway will be SET from the enolate anion of **21**, which has a lower reaction barrier, $\Delta G^*$.

# 2. Radical Cyclisation of 9 in DMSO and Benzene

Scheme S2.1. The energetics for the formation of **11** and **13** in DMSO from **21**



Scheme S2.2. The energetics for the formation of **11** and **13** in benzene from **21**



# 3. Radical Cyclisation of 15

## 3.1 The formation of products 16 and 42 from 15

Scheme S3.1. The energetics for the cyclisation of **15** in both benzene and DMSO

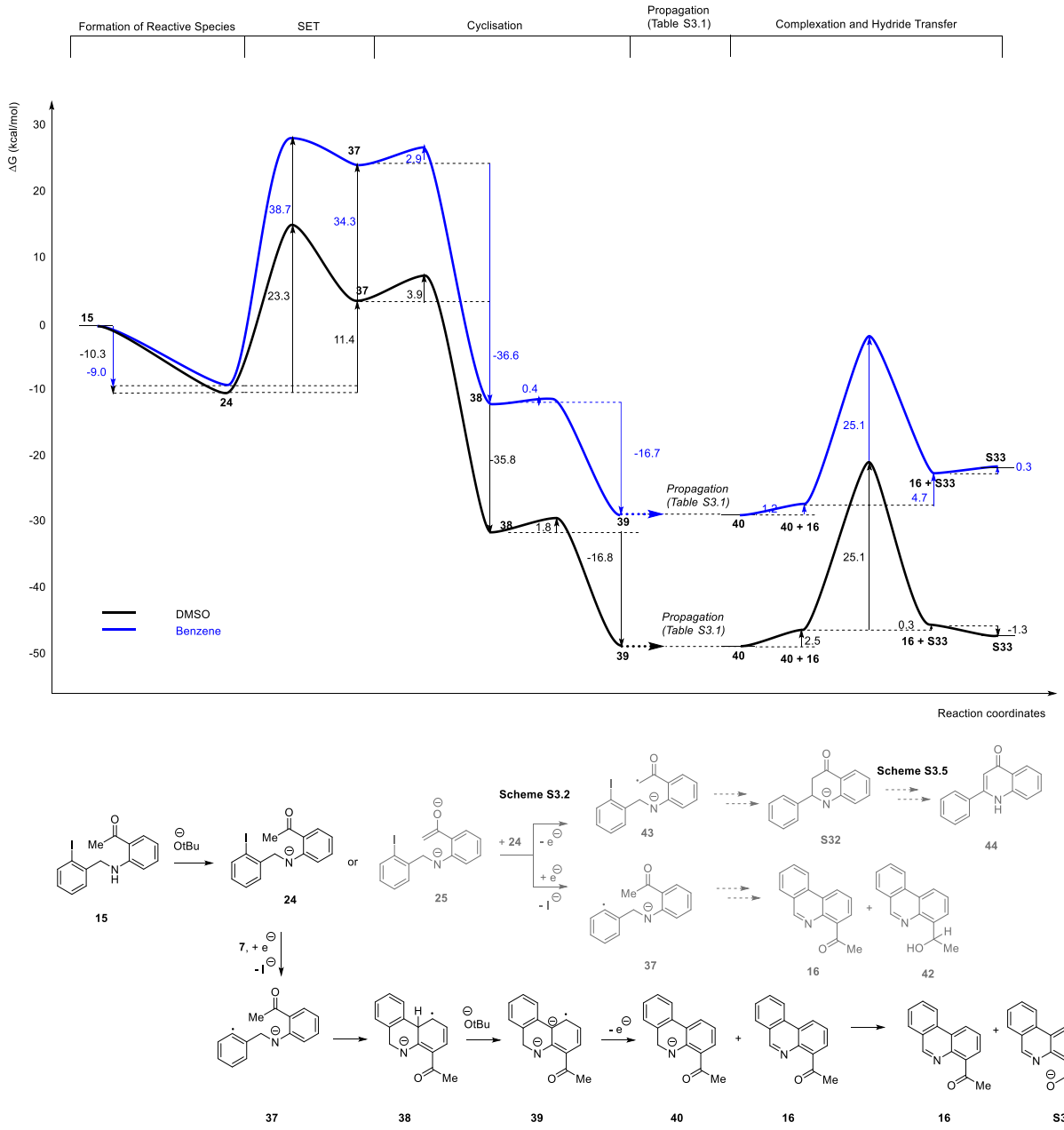
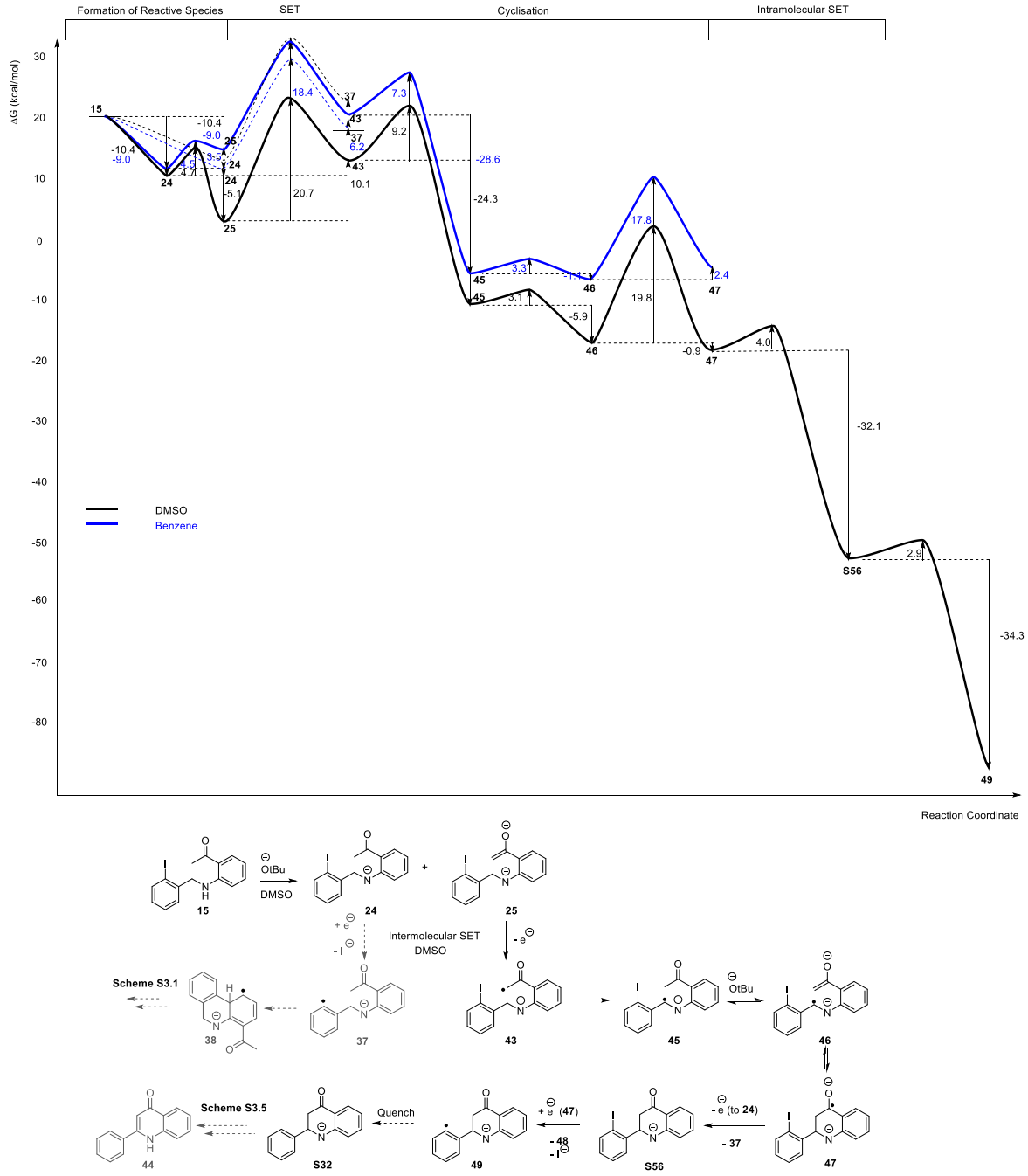


Table S3.1. The energetics for the propagation in the formation of **42**

| **Propagation** | **DMSO** | **Benzene** |
|---|---|---|
| **39** To **25** | $\Delta G^* = 3.4$<br>$\Delta G_{rxn} = -27.9$ | -- |
| **39** To **24** | $\Delta G^* = 4.5$<br>$\Delta G_{rxn} = -29.6$ | $\Delta G^* = 3.4$<br>$\Delta G_{rxn} = -33.3$ |

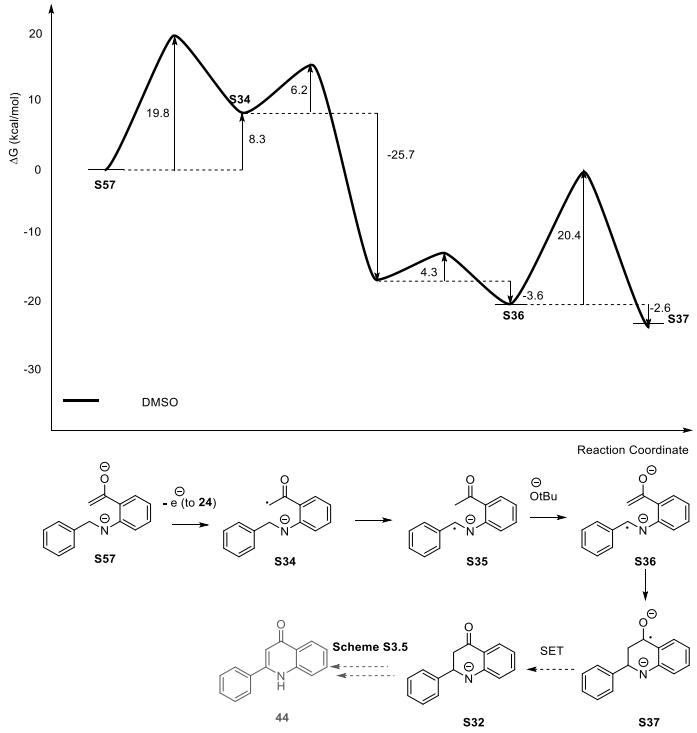
## 3.2 The formation of product 44 from 15

Scheme S3.2. The possible reaction pathway in the formation of **44**

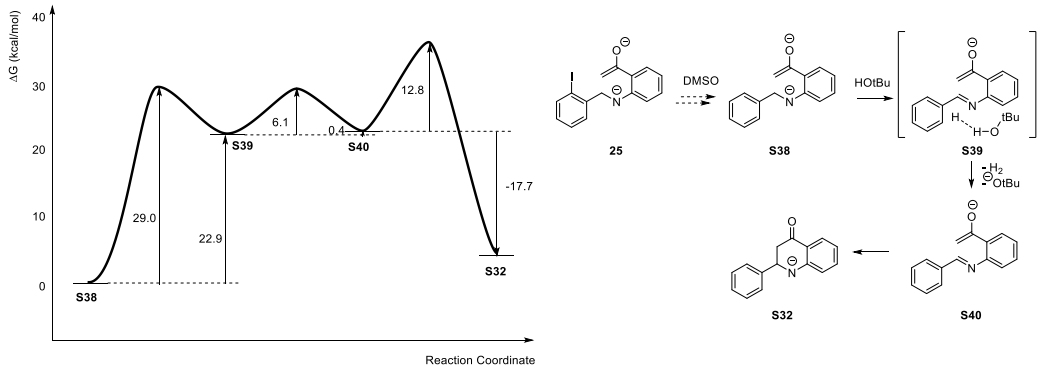



The formation of **44** occurs through tandem hydrogen atom transfer and $S_{RN}1$ cyclisation from **25** to form **S32** as an intermediate. If **25** was efficiently formed in benzene then products **44** may be formed.

Scheme S3.3: The energetics for the radical cyclisation of the non-halogenated analogues of **43**-**47** in DMSO solvent



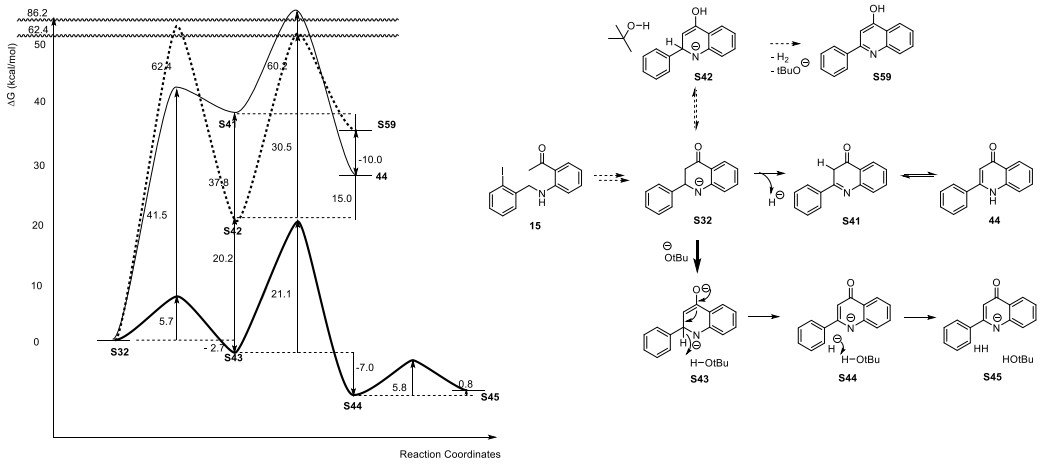

Scheme S3.4: The energetics for a possible ionic pathway to form **S32** and ultimately **44** in DMSO




The formation of **44** could also occur ionically; the deprotonated species **25** could undergo a hydride elimination to form an imine structure, analogous to **S40**. For simplicity in the computational calculation, the hydride elimination pathway was modelled using the nonhalogenated dianionic species **S38** instead of the iodinated analogue **25**. It was determined that the energetics for this hydride elimination and the ultimate cyclisation for form **S32** would be possible at high termperatures, such as 120 $^{o}$C. Therefore at the high temperature used in the reaction this pathway may be a minor pathway in the formation of **44**. However experimental results show that **44** is formed from **15** in

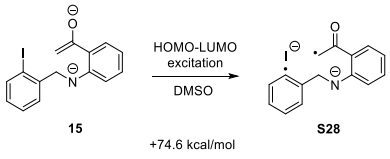
DMSO at room temperature, and therefore it is proposed that the major pathway is indeed a radical initiation followed by the reaction pathway modelled in Scheme S3.2.

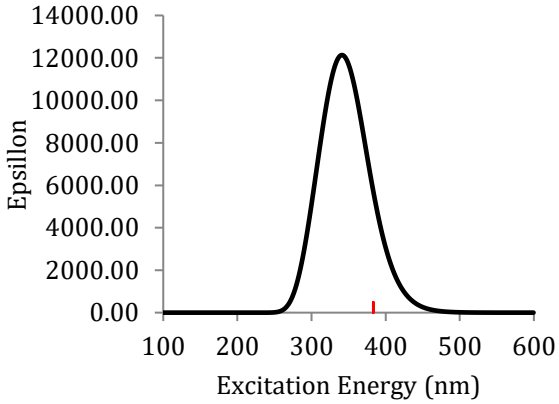
Scheme S3.5: The energetics for the formation of **44** from **S32**




## 3.3 Intramolecular Analysis of 15

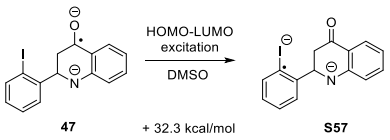
Scheme S3.6. The TDDFT calculations were performed on **15**. The Gaussian curve was generated using the default Gaussian parameters. Black lines = Overall predicted UV-vis trace. Red vertical transitions corresponds to HOMO – LUMO excitation.

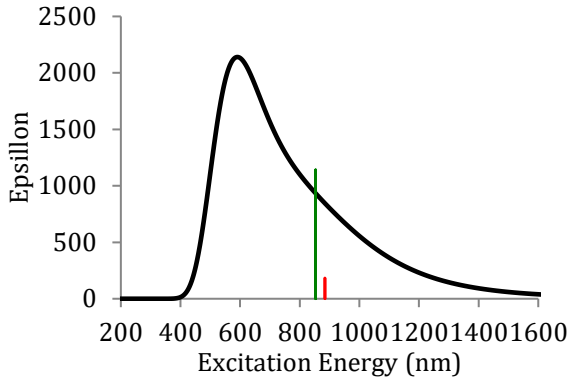


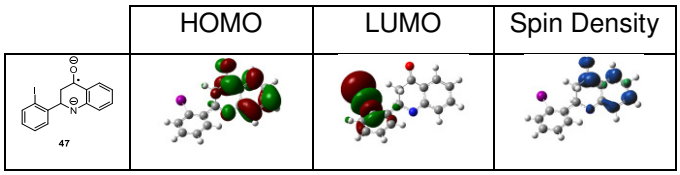



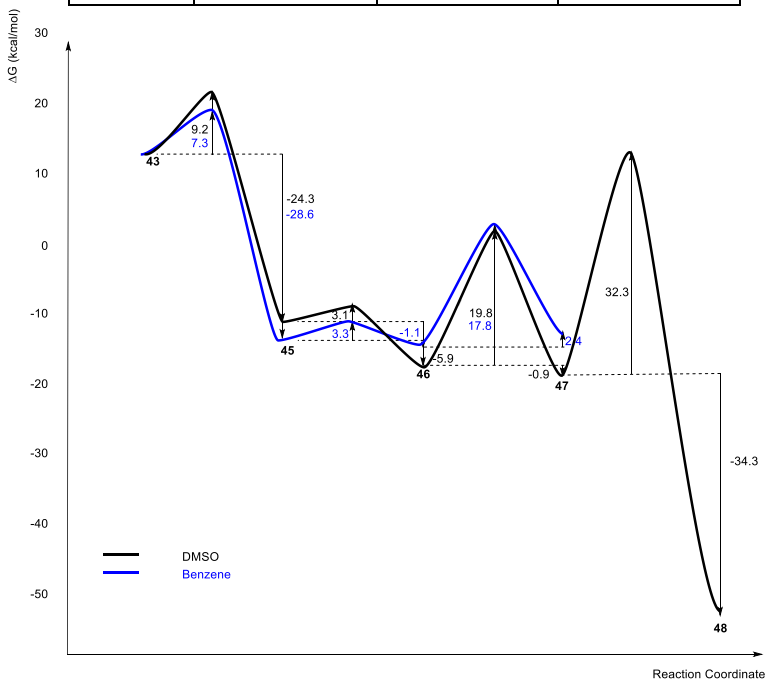

The TDDFT calculations suggests that intramolecular SET is not possible for **15** in DMSO.

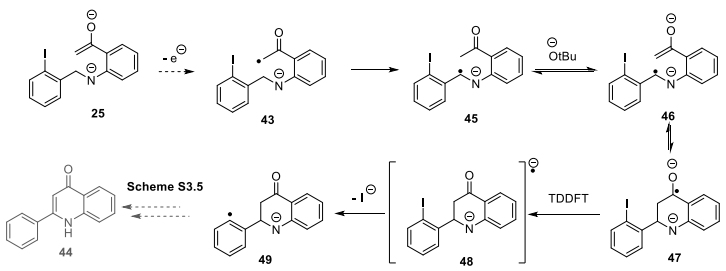
Scheme S3.7: The TDDFT calculations were performed on intermediate **47**. The Gaussian curve was generated using the default Gaussian parameters. Black lines = Overall predicted UV-Vis trace. Red and Green vertical transitions correspond to HOMO – LUMO excitations.



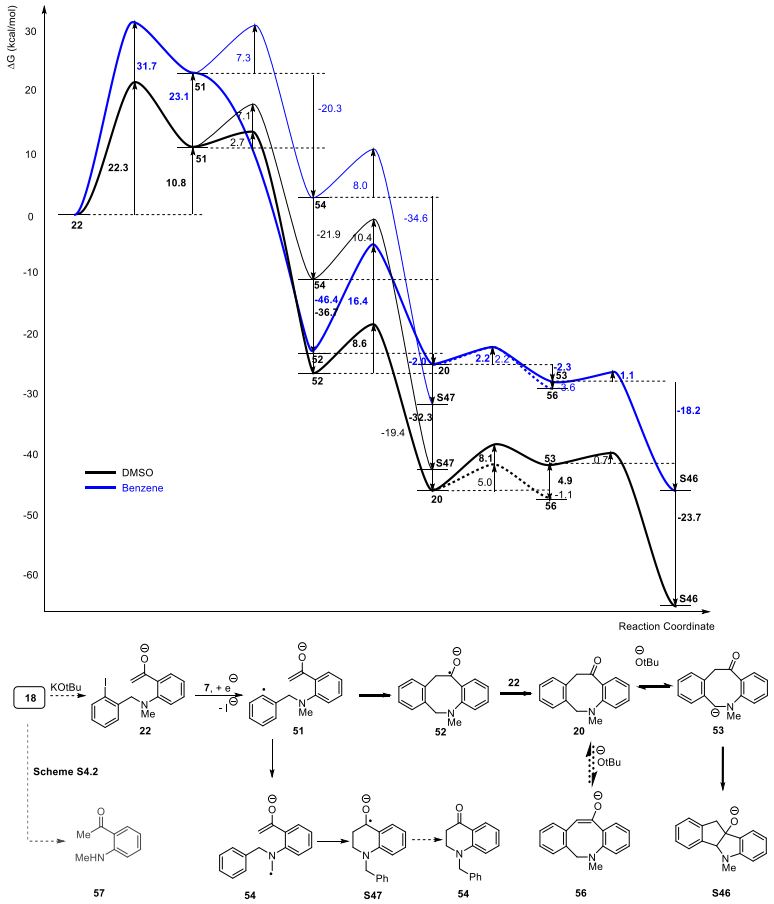



# 4. Radical Cyclisation of 18

Scheme S4.1. Cyclisation reactions of **18** in both solvents



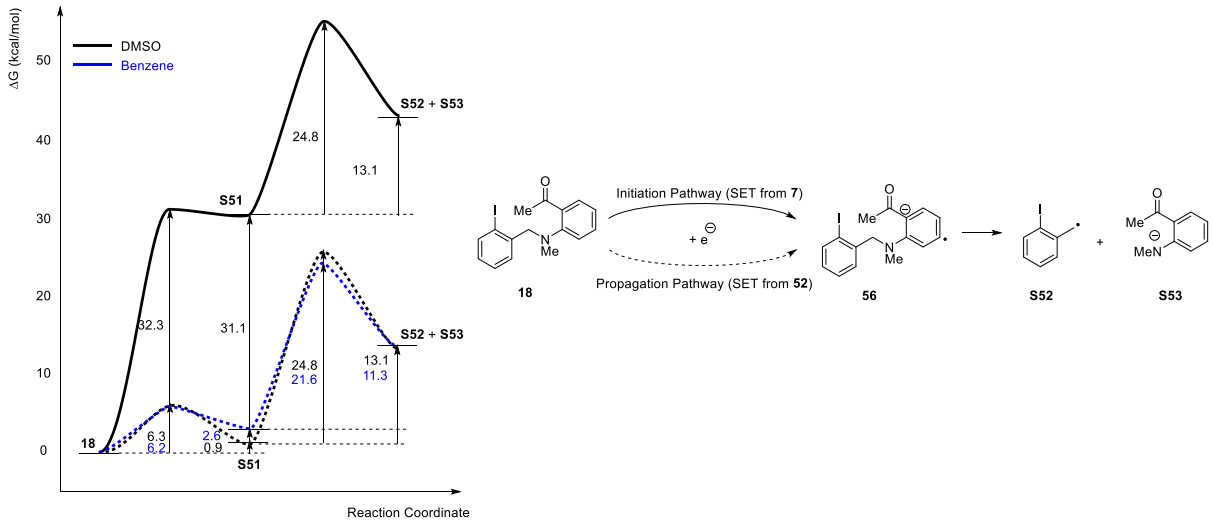

The energetics for the propagation in the formation of **20**

| **Propagation** | **DMSO** | **Benzene** |
|---|---|---|
| **52** To **22** | $\Delta G^* = 8.6$<br>$\Delta G_{rxn} = -19.4$ | $\Delta G^* = 16.4$<br>$\Delta G_{rxn} = -2.0$ |
| **52** To **18** | $\Delta G^* = 6.3$<br>$\Delta G_{rxn} = 0.9$ | $\Delta G^* = 6.2$<br>$\Delta G_{rxn} = 2.6$ |

The energetics for cyclisation from **51** in DMSO are very low barriers to either cyclise and form **52** or undergo hydrogen atom abstraction to form **54**. The formation of is more favourable and thus we expect the major product to form via intermediate **52** (e.g. product **20**) and the minor product to **55**. The energetics for the cyclisation of **51** are more defined than in DMSO. The major product will form via intermediate **52**. There may be trace amounts of **55** forming depending on the conformation of **51** upon accepting the electron, however the energetic suggest that **19** or **20** will be the predominant products. The predominant product will be predicted as **19** in benzene because the equilibrium

between **56**, **20** and **53** is evenly distributed in benzene, however in DMSO the equilibrium strongly favours the enolate product **56** which is inactive to forming **19** and hence we would expect to see some of product **20** and maybe some **19**. Experimentally we only see **20** in DMSO at room temperature, and in benzene we only see **19** when the reaction is heated.[1]

Scheme S4.2. Energetics for C-N cleavage of **18** in both solvents




The LUMO for the neutral species **18** resided on the acetophenone moiety. **18** is present in the basic reaction mixture in low amounts because of the equilibrium to form **22**. If SET occurs to this species the acetophenone moiety may result in cleavage of the C-N bond to form **S53**. The species will be only occur through the chain propagation as the energetics for the initial SET to **18** is too high and endergonic. In the propagation the DMSO solvent is more favourable for the C-N cleavage as the intermediate **S51** is more stable in DMSO than in benzene.

1. K. J. Emery; T. Tuttle; A. R. Kennedy; J. A. Murphy, Tetrahedron 2016, **72**, 7875.

# Effect of solvent on radical cyclisation pathways: $S_{RN}1$ vs. aryl-aryl bond forming mechanisms

Katie J. Emery, John A. Murphy, and Tell Tuttle

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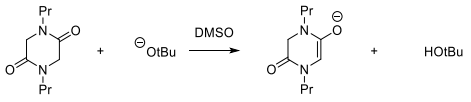
## 1. Enolate Formation




6 7

**SM: 6** + tert-butoxide anion in DMSO
46
-884.9356036

| | | | |
|---|---|---|---|
| C | -1.36374 | -0.79822 | -0.05487 |
| C | -0.09272 | -0.05446 | 0.28824 |
| C | -1.11425 | 2.07147 | -0.36904 |
| C | -2.44057 | 1.39005 | -0.08628 |
| H | 0.75743 | -0.62637 | -0.11841 |
| H | -2.70782 | 1.59702 | 0.95824 |
| H | -3.18663 | 1.86852 | -0.72031 |
| N | -0.02520 | 1.29665 | -0.25986 |
| N | -2.43981 | -0.03982 | -0.36031 |
| O | -1.08861 | 3.26245 | -0.67126 |
| O | -1.38720 | -2.02482 | -0.04216 |
| C | 1.30419 | 1.88034 | -0.44844 |
| H | 1.96759 | 1.06261 | -0.74770 |
| H | 1.23498 | 2.60439 | -1.26300 |
| C | 1.82201 | 2.56699 | 0.81368 |
| H | 1.07879 | 3.29453 | 1.15303 |
| H | 1.93685 | 1.82225 | 1.60746 |
| C | 3.15517 | 3.26223 | 0.55111 |
| H | 3.54831 | 3.72302 | 1.45897 |
| H | 3.90058 | 2.55208 | 0.18378 |
| H | 3.04047 | 4.04551 | -0.20296 |
| C | -3.73030 | -0.68246 | -0.59575 |
| H | -4.30059 | -0.04580 | -1.27767 |
| H | -3.53927 | -1.63155 | -1.09763 |
| C | -4.51247 | -0.91900 | 0.69444 |
| H | -4.68095 | 0.03770 | 1.19845 |
| H | -3.90142 | -1.53409 | 1.36132 |
| C | -5.84790 | -1.60262 | 0.41523 |
| H | -6.40277 | -1.77410 | 1.33888 |
| H | -6.46988 | -0.98996 | -0.24250 |
| H | -5.69571 | -2.56978 | -0.07064 |
| H | -0.01199 | -0.03565 | 1.38443 |
| O | 2.39950 | -1.31171 | -1.09539 |
| C | 3.27185 | -1.78200 | -0.14304 |
| C | 4.63482 | -2.15855 | -0.76476 |
| H | 5.06976 | -1.27906 | -1.25024 |
| H | 5.34989 | -2.53395 | -0.02339 |
| H | 4.48951 | -2.93105 | -1.52685 |
| C | 2.70922 | -3.03820 | 0.56209 |
| H | 1.75369 | -2.79344 | 1.03705 |
| H | 2.53016 | -3.82578 | -0.17693 |
| H | 3.38613 | -3.43163 | 1.32941 |
| C | 3.53125 | -0.71644 | 0.94931 |
| H | 3.93310 | 0.19257 | 0.49048 |
| H | 2.58925 | -0.45771 | 1.44271 |
| H | 4.23692 | -1.06021 | 1.71435 |

**TS: 6** + tert-butoxide anion in DMSO
46
-884.9266175

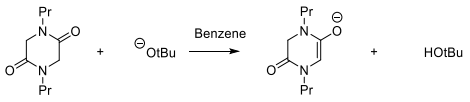
| | | | |
|---|---|---|---|
| C | 1.23006 | -0.66572 | -0.29670 |
| C | -0.06711 | 0.01566 | -0.38903 |
| C | 0.91891 | 2.07679 | 0.58258 |
| C | 2.27370 | 1.41055 | 0.46208 |
| H | -0.94805 | -0.74574 | 0.26462 |
| H | 2.77028 | 1.83917 | -0.41974 |
| H | 2.85148 | 1.71419 | 1.33721 |
| N | -0.13690 | 1.35665 | 0.19703 |
| N | 2.23191 | -0.04056 | 0.40169 |
| O | 0.85738 | 3.23008 | 1.02475 |
| O | 1.39190 | -1.80257 | -0.75824 |
| C | -1.47495 | 1.92986 | 0.31939 |
| H | -2.13978 | 1.11927 | 0.62533 |
| H | -1.45153 | 2.68310 | 1.10831 |
| C | -1.96077 | 2.56031 | -0.98390 |
| H | -1.28238 | 3.37410 | -1.25815 |
| H | -1.91255 | 1.81876 | -1.78762 |
| C | -3.38882 | 3.08008 | -0.84426 |
| H | -3.73634 | 3.54224 | -1.76993 |
| H | -4.07300 | 2.26404 | -0.59666 |
| H | -3.45615 | 3.82709 | -0.04872 |
| C | 3.50841 | -0.72514 | 0.57338 |
| H | 3.97855 | -0.32422 | 1.47739 |
| H | 3.29668 | -1.78111 | 0.74482 |
| C | 4.45489 | -0.57713 | -0.61750 |
| H | 4.68217 | 0.48083 | -0.78016 |
| H | 3.94440 | -0.94176 | -1.51305 |
| C | 5.74963 | -1.35282 | -0.39015 |
| H | 6.43184 | -1.24523 | -1.23508 |
| H | 6.26539 | -0.99608 | 0.50549 |
| H | 5.54530 | -2.41829 | -0.25570 |
| H | -0.39322 | 0.03501 | -1.43401 |
| O | -1.80671 | -1.39696 | 0.99301 |
| C | -2.85744 | -1.94263 | 0.25097 |
| C | -3.79594 | -2.70398 | 1.19560 |
| H | -4.18882 | -2.02238 | 1.95553 |
| H | -4.63994 | -3.15026 | 0.65929 |
| H | -3.24555 | -3.50199 | 1.70224 |
| C | -2.32417 | -2.91742 | -0.81328 |
| H | -1.65424 | -2.39042 | -1.49858 |
| H | -1.75431 | -3.71618 | -0.32921 |
| H | -3.13394 | -3.37030 | -1.39430 |
| C | -3.66310 | -0.83640 | -0.45592 |
| H | -4.07598 | -0.14524 | 0.28534 |
| H | -3.01488 | -0.26745 | -1.13043 |
| H | -4.49083 | -1.25020 | -1.04081 |

**Prod: 7** + tert-butanol in DMSO

46

-884.9401085

| | | | |
|---|---|---|---|
| C | 1.14689 | -0.41369 | -0.63019 |
| C | 0.02355 | 0.38278 | -0.79957 |
| C | 0.76359 | 2.09557 | 0.75506 |
| C | 2.12425 | 1.46907 | 0.51647 |
| H | -1.00391 | -0.95525 | 0.45807 |
| H | 2.55324 | 1.92962 | -0.39122 |
| H | 2.76245 | 1.72874 | 1.36193 |
| N | -0.22071 | 1.51767 | 0.05307 |
| N | 2.02432 | 0.02301 | 0.40394 |
| O | 0.61653 | 3.04921 | 1.53398 |
| O | 1.41488 | -1.47135 | -1.27037 |
| C | -1.60273 | 1.95637 | 0.21921 |
| H | -2.19976 | 1.08593 | 0.50837 |
| H | -1.62283 | 2.67453 | 1.03920 |
| C | -2.18547 | 2.59151 | -1.04083 |
| H | -1.58617 | 3.46745 | -1.30788 |
| H | -2.11666 | 1.89020 | -1.87756 |
| C | -3.64338 | 2.98825 | -0.82374 |
| H | -4.06918 | 3.44069 | -1.72084 |
| H | -4.24755 | 2.11317 | -0.56835 |
| H | -3.73514 | 3.70835 | -0.00639 |
| C | 3.28586 | -0.68931 | 0.55563 |
| H | 3.66495 | -0.48733 | 1.56442 |
| H | 3.07240 | -1.75700 | 0.49036 |
| C | 4.35838 | -0.32384 | -0.47323 |
| H | 4.64226 | 0.72689 | -0.35614 |
| H | 3.93005 | -0.43589 | -1.47329 |
| C | 5.59373 | -1.20720 | -0.32029 |
| H | 6.37197 | -0.93698 | -1.03659 |
| H | 6.01698 | -1.11448 | 0.68403 |
| H | 5.34065 | -2.25896 | -0.47916 |
| H | -0.63047 | 0.26594 | -1.64971 |
| O | -1.55898 | -1.46684 | 1.08139 |
| C | -2.51896 | -2.19660 | 0.31008 |
| C | -3.27532 | -3.07360 | 1.29873 |
| H | -3.77278 | -2.45513 | 2.04981 |
| H | -4.03160 | -3.66829 | 0.78132 |
| H | -2.58456 | -3.75127 | 1.80582 |
| C | -1.79079 | -3.04940 | -0.72779 |
| H | -1.16386 | -2.41538 | -1.36186 |
| H | -1.14303 | -3.77457 | -0.22839 |
| H | -2.50266 | -3.59085 | -1.35599 |
| C | -3.47881 | -1.22386 | -0.37907 |
| H | -3.97383 | -0.59276 | 0.36384 |
| H | -2.93594 | -0.57939 | -1.07697 |
| H | -4.24443 | -1.76722 | -0.93866 |




6 7

**SM: 6** + tert-butoxide anion in Benzene

46

-884.8938973

| | | | |
|---|---|---|---|
| C | -1.39618 | -0.79264 | -0.11444 |
| C | -0.13049 | -0.03769 | 0.21737 |
| C | -1.20083 | 2.10288 | -0.30656 |
| C | -2.50669 | 1.38004 | -0.01783 |
| H | 0.74825 | -0.56438 | -0.19831 |
| H | -2.74108 | 1.52394 | 1.04624 |
| H | -3.28000 | 1.88558 | -0.59651 |
| N | -0.10268 | 1.33560 | -0.28116 |
| N | -2.49228 | -0.02874 | -0.37690 |
| O | -1.21463 | 3.30820 | -0.54112 |
| O | -1.42552 | -2.01376 | -0.12304 |
| C | 1.21796 | 1.92645 | -0.51275 |
| H | 1.84290 | 1.15049 | -0.96639 |
| H | 1.08461 | 2.77144 | -1.19000 |
| C | 1.86860 | 2.38342 | 0.79069 |
| H | 1.21575 | 3.10350 | 1.29540 |
| H | 1.97959 | 1.51231 | 1.44470 |
| C | 3.24063 | 2.99575 | 0.52403 |
| H | 3.73371 | 3.29395 | 1.45188 |
| H | 3.88349 | 2.27399 | 0.01364 |
| H | 3.15541 | 3.88096 | -0.11289 |
| C | -3.77427 | -0.68456 | -0.59507 |
| H | -4.37597 | -0.04033 | -1.24393 |
| H | -3.57872 | -1.61646 | -1.12704 |
| C | -4.52281 | -0.97723 | 0.70435 |
| H | -4.69956 | -0.04045 | 1.24278 |
| H | -3.88277 | -1.60034 | 1.33533 |
| C | -5.84992 | -1.68081 | 0.43457 |
| H | -6.38586 | -1.88805 | 1.36246 |
| H | -6.49687 | -1.06612 | -0.19749 |
| H | -5.68593 | -2.63182 | -0.07849 |
| H | -0.02987 | -0.05267 | 1.31270 |
| O | 2.61202 | -0.79913 | -0.85451 |
| C | 3.37217 | -1.65499 | -0.11138 |
| C | 4.77097 | -1.85500 | -0.74207 |
| H | 5.27232 | -0.88494 | -0.82074 |
| H | 5.40936 | -2.53489 | -0.16357 |
| H | 4.65333 | -2.25778 | -1.75283 |
| C | 2.69914 | -3.04446 | 0.00384 |
| H | 1.70911 | -2.92993 | 0.45651 |
| H | 2.56263 | -3.46137 | -0.99867 |
| H | 3.28128 | -3.75494 | 0.60446 |
| C | 3.57453 | -1.11114 | 1.32604 |
| H | 4.05753 | -0.12954 | 1.27470 |
| H | 2.59594 | -0.98162 | 1.80090 |
| H | 4.18427 | -1.77092 | 1.95623 |

**TS: 6** + tert-butoxide anion in Benzene

46

-884.8883013

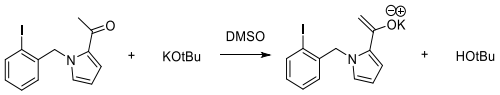
| | | | |
|---|---|---|---|
| C | 1.22521 | -0.65288 | -0.28132 |
| C | -0.08105 | 0.01670 | -0.36513 |
| C | 0.89037 | 2.10184 | 0.57550 |
| C | 2.25095 | 1.43772 | 0.48029 |
| H | -0.93544 | -0.70658 | 0.29578 |
| H | 2.76196 | 1.87196 | -0.39152 |
| H | 2.80656 | 1.75090 | 1.36702 |
| N | -0.15883 | 1.36540 | 0.20052 |
| N | 2.22196 | -0.01214 | 0.42225 |
| O | 0.82418 | 3.26265 | 0.98886 |
| O | 1.40595 | -1.77596 | -0.75255 |
| C | -1.50267 | 1.92196 | 0.32519 |
| H | -2.15563 | 1.10086 | 0.63238 |
| H | -1.48448 | 2.67684 | 1.11318 |
| C | -1.99198 | 2.54802 | -0.97933 |
| H | -1.32529 | 3.37366 | -1.24719 |
| H | -1.92777 | 1.80747 | -1.78309 |
| C | -3.42989 | 3.04209 | -0.84751 |
| H | -3.78358 | 3.49787 | -1.77474 |
| H | -4.09848 | 2.21278 | -0.60163 |
| H | -3.51391 | 3.78766 | -0.05191 |
| C | 3.49929 | -0.69049 | 0.58130 |
| H | 3.99101 | -0.26993 | 1.46571 |
| H | 3.28983 | -1.74276 | 0.77918 |
| C | 4.41967 | -0.57634 | -0.63452 |
| H | 4.63464 | 0.47731 | -0.83981 |
| H | 3.88837 | -0.97848 | -1.50090 |
| C | 5.72485 | -1.33555 | -0.41087 |
| H | 6.38520 | -1.26231 | -1.27722 |
| H | 6.26317 | -0.94157 | 0.45604 |
| H | 5.52776 | -2.39512 | -0.22739 |
| H | -0.41152 | 0.02039 | -1.40933 |
| O | -1.86816 | -1.31424 | 1.04334 |
| C | -2.80641 | -1.96183 | 0.25373 |
| C | -3.76147 | -2.76322 | 1.15209 |
| H | -4.25230 | -2.08765 | 1.85865 |
| H | -4.53052 | -3.28837 | 0.57368 |
| H | -3.18982 | -3.49827 | 1.72532 |
| C | -2.12251 | -2.93133 | -0.73038 |
| H | -1.41784 | -2.38824 | -1.36632 |
| H | -1.55024 | -3.67512 | -0.16882 |
| H | -2.84772 | -3.45082 | -1.36720 |
| C | -3.63813 | -0.94180 | -0.55412 |
| H | -4.14304 | -0.25787 | 0.13553 |
| H | -2.98134 | -0.34971 | -1.20018 |
| H | -4.39451 | -1.42668 | -1.18135 |

**Prod: 7** + tert-butanol in Benzene

46

-884.9027601

| | | | |
|---|---|---|---|
| C | 1.13092 | -0.42327 | -0.57318 |
| C | -0.01873 | 0.34347 | -0.73148 |
| C | 0.76417 | 2.15701 | 0.69671 |
| C | 2.12179 | 1.51482 | 0.47058 |
| H | -1.06328 | -0.92885 | 0.58418 |
| H | 2.53997 | 1.93654 | -0.46145 |
| H | 2.76556 | 1.81760 | 1.29789 |
| N | -0.23746 | 1.52525 | 0.06489 |
| N | 2.02453 | 0.06660 | 0.42709 |
| O | 0.63498 | 3.16361 | 1.40370 |
| O | 1.41159 | -1.48347 | -1.19009 |
| C | -1.61148 | 1.97116 | 0.24906 |
| H | -2.21135 | 1.10156 | 0.53725 |
| H | -1.61910 | 2.68790 | 1.07168 |
| C | -2.19735 | 2.61597 | -1.00546 |
| H | -1.59376 | 3.49044 | -1.26770 |
| H | -2.12864 | 1.91674 | -1.84432 |
| C | -3.65342 | 3.01803 | -0.78650 |
| H | -4.08041 | 3.47946 | -1.67922 |
| H | -4.26116 | 2.14403 | -0.53546 |
| H | -3.74079 | 3.73208 | 0.03703 |
| C | 3.28122 | -0.64507 | 0.58501 |
| H | 3.69494 | -0.38537 | 1.56768 |
| H | 3.05353 | -1.71215 | 0.58958 |
| C | 4.32336 | -0.36289 | -0.50106 |
| H | 4.62083 | 0.69078 | -0.46765 |
| H | 3.85512 | -0.54364 | -1.47216 |
| C | 5.55340 | -1.25003 | -0.32907 |
| H | 6.30928 | -1.04780 | -1.09123 |
| H | 6.01562 | -1.09424 | 0.65068 |
| H | 5.27729 | -2.30565 | -0.40140 |
| H | -0.63130 | 0.23869 | -1.61453 |
| O | -1.69559 | -1.42037 | 1.15078 |
| C | -2.48851 | -2.23700 | 0.29412 |
| C | -3.34335 | -3.10220 | 1.21267 |
| H | -3.96805 | -2.47144 | 1.85030 |
| H | -3.99062 | -3.76182 | 0.62850 |
| H | -2.70257 | -3.71375 | 1.85203 |
| C | -1.57795 | -3.10283 | -0.57624 |
| H | -0.89223 | -2.47698 | -1.15578 |
| H | -0.97083 | -3.75437 | 0.05771 |
| H | -2.16609 | -3.72500 | -1.25758 |
| C | -3.38549 | -1.35412 | -0.58003 |
| H | -4.00992 | -0.71596 | 0.05150 |
| H | -2.77539 | -0.71418 | -1.22283 |
| H | -4.03540 | -1.96402 | -1.21430 |




9 21-K

**SM: 9** + KOtBu in DMSO
43
-1476.8805597

| | | | |
|---|---|---|---|
| C | 2.99260 | 3.09117 | 0.30629 |
| C | 1.77409 | 2.60178 | -0.14970 |
| C | 1.56689 | 1.23348 | -0.34423 |
| C | 2.63292 | 0.37619 | -0.06828 |
| C | 3.85940 | 0.84823 | 0.38589 |
| C | 4.03708 | 2.21470 | 0.57661 |
| H | 3.12341 | 4.15670 | 0.45115 |
| H | 0.96311 | 3.29269 | -0.35462 |
| H | 4.66819 | 0.15894 | 0.59302 |
| H | 4.98965 | 2.58491 | 0.93600 |
| C | 0.23890 | 0.70540 | -0.84491 |
| H | 0.33094 | 0.43854 | -1.90144 |
| H | -0.09460 | -0.19914 | -0.33171 |
| N | -0.83132 | 1.69123 | -0.75556 |
| C | -1.26080 | 2.40364 | -1.83278 |
| C | -1.48578 | 2.15428 | 0.37703 |
| C | -2.21575 | 3.31691 | -1.42423 |
| H | -0.85219 | 2.20398 | -2.81191 |
| C | -2.35107 | 3.16182 | -0.03176 |
| H | -3.00830 | 3.70254 | 0.63079 |
| H | -2.74314 | 4.00733 | -2.06272 |
| C | -1.35501 | 1.68906 | 1.77753 |
| C | -0.48007 | 0.52331 | 2.13665 |
| H | 0.56807 | 0.73940 | 1.91492 |
| H | -0.58994 | 0.32750 | 3.20222 |
| O | -2.01063 | 2.26729 | 2.63021 |
| I | 2.42185 | -1.73049 | -0.33134 |
| H | -0.79997 | -0.34535 | 1.54695 |
| K | -3.58614 | 0.31131 | -1.01592 |
| O | -1.92862 | -1.30645 | -0.07269 |
| C | -2.23009 | -2.59811 | 0.31063 |
| C | -3.75891 | -2.81164 | 0.35887 |
| H | -4.20851 | -2.08983 | 1.04930 |
| H | -4.18860 | -2.65414 | -0.63695 |
| H | -4.03514 | -3.81902 | 0.68810 |
| C | -1.66135 | -2.90621 | 1.71170 |
| H | -1.88061 | -3.92989 | 2.03437 |
| H | -0.57472 | -2.76981 | 1.70470 |
| H | -2.08506 | -2.21380 | 2.44617 |
| C | -1.63862 | -3.62260 | -0.67942 |
| H | -2.03503 | -3.43610 | -1.68247 |
| H | -0.55057 | -3.51118 | -0.71615 |
| H | -1.87172 | -4.65690 | -0.40237 |

**TS: 9** + KOtBu in DMSO
43
-1476.8690869

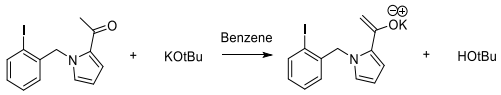
| | | | |
|---|---|---|---|
| C | -2.56786 | -3.30761 | 0.64319 |
| C | -1.43416 | -2.70114 | 0.11504 |
| C | -1.41646 | -1.33832 | -0.19343 |
| C | -2.58472 | -0.61141 | 0.03769 |
| C | -3.72697 | -1.20108 | 0.56700 |
| C | -3.71504 | -2.55778 | 0.87375 |
| H | -2.55210 | -4.36566 | 0.87481 |
| H | -0.54191 | -3.29266 | -0.05930 |
| H | -4.61791 | -0.61087 | 0.73992 |
| H | -4.60256 | -3.01904 | 1.28954 |
| C | -0.17753 | -0.68224 | -0.77153 |
| H | -0.36203 | -0.41327 | -1.81512 |
| N | 0.98402 | -1.55991 | -0.75946 |
| C | 1.36485 | -2.25926 | -1.87126 |
| C | 1.76433 | -1.96354 | 0.31720 |
| C | 2.40782 | -3.09838 | -1.53987 |
| H | 0.85784 | -2.10104 | -2.81099 |
| C | 2.65457 | -2.91203 | -0.16164 |
| H | 3.40776 | -3.39048 | 0.44376 |
| H | 2.92442 | -3.76064 | -2.21627 |
| C | 1.76942 | -1.44287 | 1.72276 |
| C | 0.94129 | -0.31644 | 2.08699 |
| H | -0.08975 | -0.34776 | 1.74287 |
| H | 1.01257 | -0.09266 | 3.15020 |
| O | 2.62799 | -1.92995 | 2.46977 |
| I | -2.67849 | 1.46645 | -0.43685 |
| H | 1.53772 | 0.60828 | 1.34878 |
| K | 3.56041 | 0.02389 | -1.22165 |
| O | 2.20259 | 1.34032 | 0.47780 |
| C | 1.91231 | 2.71184 | 0.45752 |
| C | 3.19678 | 3.51193 | 0.71354 |
| H | 3.60581 | 3.25321 | 1.69419 |
| H | 3.94485 | 3.26542 | -0.04629 |
| H | 3.01723 | 4.59124 | 0.68464 |
| C | 0.87718 | 3.05980 | 1.53812 |
| H | 0.63803 | 4.12722 | 1.52874 |
| H | -0.04566 | 2.49633 | 1.37117 |
| H | 1.26244 | 2.79856 | 2.52804 |
| C | 1.34811 | 3.09551 | -0.91869 |
| H | 2.08344 | 2.87689 | -1.69973 |
| H | 0.44386 | 2.51545 | -1.12516 |
| H | 1.09774 | 4.15975 | -0.97469 |
| H | 0.07425 | 0.24035 | -0.24774 |

**Prod: 21-K** + HOtBu in DMSO

43

-1476.8930435

| | | | |
|---|---|---|---|
| C | -2.96084 | -3.04404 | 1.01082 |
| C | -1.82388 | -2.55495 | 0.37817 |
| C | -1.74772 | -1.22894 | -0.05459 |
| C | -2.85587 | -0.41336 | 0.17515 |
| C | -4.00170 | -0.88480 | 0.80515 |
| C | -4.05229 | -2.21006 | 1.22475 |
| H | -2.99171 | -4.07676 | 1.33658 |
| H | -0.97265 | -3.20798 | 0.21855 |
| H | -4.84623 | -0.22730 | 0.96808 |
| H | -4.94346 | -2.58151 | 1.71597 |
| C | -0.50634 | -0.70158 | -0.75056 |
| H | -0.76781 | -0.38266 | -1.76306 |
| H | -0.12085 | 0.17582 | -0.22809 |
| N | 0.54980 | -1.68797 | -0.86278 |
| C | 0.63560 | -2.53610 | -1.93682 |
| C | 1.55299 | -1.99056 | 0.04217 |
| C | 1.69962 | -3.38535 | -1.74582 |
| H | -0.06681 | -2.44928 | -2.75184 |
| C | 2.28327 | -3.03367 | -0.50270 |
| H | 3.14005 | -3.48588 | -0.02761 |
| H | 2.02176 | -4.15842 | -2.42582 |
| C | 1.87572 | -1.31029 | 1.34398 |
| C | 0.91766 | -0.62637 | 2.05174 |
| H | -0.13251 | -0.65781 | 1.80157 |
| H | 1.20400 | -0.16017 | 2.98821 |
| O | 3.11608 | -1.40284 | 1.67868 |
| I | -2.83969 | 1.63040 | -0.44238 |
| H | 1.92967 | 0.79065 | 0.64135 |
| K | 4.43165 | -0.56019 | -0.39826 |
| O | 2.45681 | 1.24655 | -0.04132 |
| C | 2.38755 | 2.65734 | 0.21428 |
| C | 3.00747 | 2.94510 | 1.58049 |
| H | 2.45581 | 2.41873 | 2.36509 |
| H | 4.04652 | 2.60723 | 1.59987 |
| H | 2.98312 | 4.01488 | 1.80119 |
| C | 0.92466 | 3.09248 | 0.17971 |
| H | 0.83246 | 4.16707 | 0.35525 |
| H | 0.48343 | 2.85569 | -0.79181 |
| H | 0.35366 | 2.56846 | 0.95306 |
| C | 3.18335 | 3.32648 | -0.89657 |
| H | 4.21826 | 2.97560 | -0.88525 |
| H | 2.74469 | 3.09392 | -1.86960 |
| H | 3.18348 | 4.41039 | -0.76395 |




9 21-K

**SM: 9** + KOtBu in Benzene

43

-1476.8655305

| | | | |
|---|---|---|---|
| C | -2.77192 | -3.27213 | 0.02960 |
| C | -1.57793 | -2.66482 | -0.33941 |
| C | -1.46042 | -1.27384 | -0.41514 |
| C | -2.59263 | -0.51631 | -0.10978 |
| C | -3.79514 | -1.10849 | 0.25949 |
| C | -3.88315 | -2.49414 | 0.33132 |
| H | -2.83066 | -4.35244 | 0.08318 |
| H | -0.71493 | -3.28075 | -0.56966 |
| H | -4.65540 | -0.49441 | 0.49425 |
| H | -4.81782 | -2.95659 | 0.62465 |
| C | -0.15708 | -0.62125 | -0.82804 |
| H | -0.22578 | -0.29066 | -1.86841 |
| H | 0.10301 | 0.26892 | -0.25227 |
| N | 0.97121 | -1.54298 | -0.75424 |
| C | 1.47945 | -2.16983 | -1.85020 |
| C | 1.58582 | -2.05126 | 0.37742 |
| C | 2.44465 | -3.07682 | -1.44929 |
| H | 1.10537 | -1.92832 | -2.83352 |
| C | 2.50361 | -3.00549 | -0.04286 |
| H | 3.13761 | -3.56704 | 0.62545 |
| H | 3.01910 | -3.71740 | -2.09967 |
| C | 1.39350 | -1.65692 | 1.79984 |
| C | 0.48931 | -0.52046 | 2.17933 |
| H | -0.54673 | -0.73506 | 1.90480 |
| H | 0.55523 | -0.37834 | 3.25663 |
| O | 2.03495 | -2.26410 | 2.63704 |
| I | -2.52796 | 1.61153 | -0.19130 |
| H | 0.82217 | 0.37827 | 1.64458 |
| K | 3.75418 | -0.19431 | -0.67866 |
| O | 1.99216 | 1.31562 | -0.01090 |
| C | 2.01282 | 2.68596 | 0.14769 |
| C | 3.46592 | 3.20069 | 0.24050 |
| H | 3.97266 | 2.71532 | 1.08160 |
| H | 4.00533 | 2.95382 | -0.68186 |
| H | 3.52579 | 4.28500 | 0.38276 |
| C | 1.27197 | 3.09813 | 1.43493 |
| H | 1.26724 | 4.18259 | 1.58832 |
| H | 0.23542 | 2.75010 | 1.38445 |
| H | 1.74741 | 2.62696 | 2.30110 |
| C | 1.33279 | 3.37988 | -1.04911 |
| H | 1.86337 | 3.12233 | -1.97161 |
| H | 0.30410 | 3.01914 | -1.13754 |
| H | 1.31547 | 4.47099 | -0.95096 |

**TS: 9** + KOtBu in Benzene

43

-1476.8560457

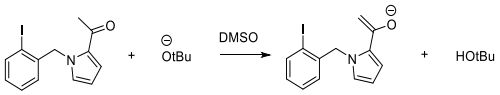
| | | | |
|---|---|---|---|
| C | 2.09652 | 2.65334 | 2.21905 |
| C | 1.16452 | 2.35845 | 1.23231 |
| C | 1.34008 | 1.27858 | 0.36248 |
| C | 2.49812 | 0.51426 | 0.51355 |
| C | 3.44225 | 0.79754 | 1.49453 |
| C | 3.23667 | 1.87033 | 2.35398 |
| H | 1.93020 | 3.49537 | 2.87981 |
| H | 0.27731 | 2.97418 | 1.12699 |
| H | 4.33358 | 0.18972 | 1.58326 |
| H | 3.97176 | 2.09084 | 3.11864 |
| C | 0.30186 | 0.95900 | -0.69711 |
| H | 0.80100 | 0.75475 | -1.64634 |
| N | -0.63445 | 2.04739 | -0.92813 |
| C | -0.33958 | 3.07903 | -1.77214 |
| C | -1.91987 | 2.21980 | -0.44443 |
| C | -1.42009 | 3.93100 | -1.83697 |
| H | 0.61582 | 3.11157 | -2.27373 |
| C | -2.42153 | 3.38031 | -1.00763 |
| H | -3.40606 | 3.77201 | -0.80678 |
| H | -1.47597 | 4.83515 | -2.42203 |
| C | -2.64113 | 1.38280 | 0.54537 |
| C | -1.93812 | 0.49991 | 1.44806 |
| H | -0.90806 | 0.76060 | 1.67508 |
| H | -2.52193 | 0.30907 | 2.34891 |
| O | -3.88529 | 1.43002 | 0.50991 |
| I | 2.92323 | -1.11913 | -0.79373 |
| H | -1.98229 | -0.63519 | 0.80826 |
| K | -4.64268 | -1.03584 | 0.08312 |
| O | -2.26875 | -1.75391 | 0.12468 |
| C | -1.35067 | -2.80312 | 0.24772 |
| C | -2.09168 | -4.07991 | 0.66902 |
| H | -2.57736 | -3.92449 | 1.63686 |
| H | -2.86105 | -4.31958 | -0.07132 |
| H | -1.41614 | -4.93683 | 0.75369 |
| C | -0.29140 | -2.47064 | 1.31223 |
| H | 0.43486 | -3.28152 | 1.41907 |
| H | 0.25680 | -1.56135 | 1.04750 |
| H | -0.77267 | -2.30287 | 2.28041 |
| C | -0.66438 | -3.04461 | -1.10348 |
| H | -1.41321 | -3.31860 | -1.85217 |
| H | -0.16685 | -2.13049 | -1.43682 |
| H | 0.08323 | -3.84246 | -1.04654 |
| H | -0.25885 | 0.05800 | -0.43341 |

**Prod: 21-K** + KOtBu in Benzene

43

-1476.8753977

| | | | |
|---|---|---|---|
| C | -2.87504 | -3.03826 | 1.12095 |
| C | -1.75486 | -2.54210 | 0.46570 |
| C | -1.71551 | -1.22900 | -0.00862 |
| C | -2.84131 | -0.43438 | 0.20409 |
| C | -3.97104 | -0.91357 | 0.85594 |
| C | -3.98510 | -2.22553 | 1.31682 |
| H | -2.87655 | -4.05988 | 1.48087 |
| H | -0.88679 | -3.17673 | 0.32361 |
| H | -4.82994 | -0.27151 | 1.00408 |
| H | -4.86300 | -2.60327 | 1.82688 |
| C | -0.48928 | -0.69187 | -0.72335 |
| H | -0.77124 | -0.35504 | -1.72456 |
| H | -0.09034 | 0.17344 | -0.19050 |
| N | 0.56189 | -1.67755 | -0.87244 |
| C | 0.61490 | -2.52508 | -1.94976 |
| C | 1.58319 | -1.98757 | 0.00772 |
| C | 1.67817 | -3.38030 | -1.78634 |
| H | -0.11034 | -2.43596 | -2.74419 |
| C | 2.29396 | -3.03436 | -0.55673 |
| H | 3.14464 | -3.50407 | -0.08737 |
| H | 1.97291 | -4.15970 | -2.47136 |
| C | 1.94701 | -1.31355 | 1.30454 |
| C | 1.02088 | -0.61204 | 2.03611 |
| H | -0.03846 | -0.64375 | 1.82811 |
| H | 1.34100 | -0.18301 | 2.97914 |
| O | 3.19423 | -1.42168 | 1.59894 |
| I | -2.88343 | 1.58853 | -0.47933 |
| H | 2.11297 | 0.83061 | 0.77011 |
| K | 4.40094 | -0.57347 | -0.42901 |
| O | 2.65529 | 1.32088 | 0.11914 |
| C | 2.36211 | 2.71845 | 0.24929 |
| C | 2.82161 | 3.19758 | 1.62502 |
| H | 2.29364 | 2.64980 | 2.41046 |
| H | 3.89377 | 3.02629 | 1.74589 |
| H | 2.62024 | 4.26392 | 1.75272 |
| C | 0.85960 | 2.92887 | 0.08068 |
| H | 0.60326 | 3.98883 | 0.15283 |
| H | 0.53015 | 2.55493 | -0.89224 |
| H | 0.31134 | 2.39128 | 0.86076 |
| C | 3.13773 | 3.41573 | -0.85911 |
| H | 4.20869 | 3.22755 | -0.74786 |
| H | 2.81445 | 3.04690 | -1.83535 |
| H | 2.97178 | 4.49441 | -0.82191 |




9 21

**SM: 9** + tert-butoxide anion in DMSO
42
-876.9881769

| | | | |
|---|---|---|---|
| C | 3.51999 | 1.86939 | 0.74825 |
| C | 2.28579 | 1.87535 | 0.10880 |
| C | 1.61787 | 0.68651 | -0.20105 |
| C | 2.25041 | -0.50898 | 0.14465 |
| C | 3.48496 | -0.53420 | 0.78385 |
| C | 4.12095 | 0.66408 | 1.09066 |
| H | 4.00980 | 2.80795 | 0.97760 |
| H | 1.82594 | 2.82225 | -0.15280 |
| H | 3.94827 | -1.47810 | 1.04199 |
| H | 5.08048 | 0.64728 | 1.59307 |
| C | 0.27021 | 0.70267 | -0.89719 |
| H | 0.38892 | 0.31795 | -1.91410 |
| H | -0.47729 | 0.06019 | -0.41962 |
| N | -0.27630 | 2.04806 | -1.02282 |
| C | -0.12070 | 2.78828 | -2.15166 |
| C | -0.85751 | 2.84309 | -0.04548 |
| C | -0.61279 | 4.06230 | -1.93643 |
| H | 0.32904 | 2.34807 | -3.02880 |
| C | -1.07502 | 4.09408 | -0.60863 |
| H | -1.53512 | 4.92050 | -0.09011 |
| H | -0.63938 | 4.86051 | -2.66096 |
| C | -1.20193 | 2.48612 | 1.34540 |
| C | -0.97248 | 1.10061 | 1.87641 |
| H | 0.08644 | 0.83353 | 1.82704 |
| H | -1.30447 | 1.07164 | 2.91350 |
| O | -1.70633 | 3.34934 | 2.05120 |
| I | 1.34734 | -2.38779 | -0.31158 |
| H | -1.54320 | 0.38371 | 1.26423 |
| O | -2.52358 | -0.55540 | -0.34453 |
| C | -3.39011 | -1.54086 | 0.06698 |
| C | -4.86302 | -1.11899 | -0.13705 |
| H | -5.06636 | -0.20359 | 0.42777 |
| H | -5.04187 | -0.91213 | -1.19698 |
| H | -5.57180 | -1.88928 | 0.18824 |
| C | -3.19405 | -1.85761 | 1.56806 |
| H | -3.85972 | -2.65376 | 1.92043 |
| H | -2.15779 | -2.16696 | 1.74411 |
| H | -3.38538 | -0.95952 | 2.16423 |
| C | -3.16634 | -2.85061 | -0.72203 |
| H | -3.30423 | -2.66091 | -1.79131 |
| H | -2.14127 | -3.20239 | -0.56831 |
| H | -3.85413 | -3.64912 | -0.42051 |

**TS: 9** + tert-butoxide anion in DMSO
42
-876.9818173

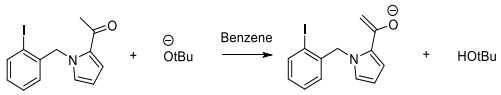
| | | | |
|---|---|---|---|
| C | 0.34025 | -2.76997 | 2.42937 |
| C | 0.89692 | -2.10487 | 1.34366 |
| C | 0.09849 | -1.47341 | 0.38609 |
| C | -1.28486 | -1.55056 | 0.55469 |
| C | -1.85981 | -2.21014 | 1.63589 |
| C | -1.04076 | -2.81938 | 2.58046 |
| H | 0.98673 | -3.24798 | 3.15534 |
| H | 1.97545 | -2.06658 | 1.23046 |
| H | -2.93655 | -2.25428 | 1.73918 |
| H | -1.48767 | -3.33298 | 3.42307 |
| C | 0.71744 | -0.72736 | -0.78031 |
| H | 0.25990 | -1.07244 | -1.71030 |
| N | 2.15121 | -0.94864 | -0.90542 |
| C | 2.64809 | -2.02992 | -1.57524 |
| C | 3.20867 | -0.18589 | -0.43812 |
| C | 4.02497 | -1.98523 | -1.54662 |
| H | 1.97408 | -2.73893 | -2.03224 |
| C | 4.37627 | -0.81598 | -0.83569 |
| H | 5.36675 | -0.45428 | -0.60871 |
| H | 4.69081 | -2.70722 | -1.99276 |
| C | 3.16155 | 1.04445 | 0.40365 |
| C | 1.97069 | 1.36582 | 1.16993 |
| H | 1.43272 | 0.49770 | 1.54940 |
| H | 2.19943 | 2.07877 | 1.96293 |
| O | 4.16774 | 1.76387 | 0.38606 |
| I | -2.61648 | -0.70614 | -0.88686 |
| H | 1.15486 | 1.95563 | 0.38802 |
| O | 0.22746 | 2.53640 | -0.46108 |
| C | -0.64879 | 3.36417 | 0.23885 |
| C | 0.07228 | 4.64889 | 0.68691 |
| H | 0.92735 | 4.38976 | 1.31862 |
| H | 0.44607 | 5.18675 | -0.18958 |
| H | -0.58570 | 5.31812 | 1.25123 |
| C | -1.20152 | 2.64989 | 1.48907 |
| H | -1.92067 | 3.27555 | 2.02789 |
| H | -1.70247 | 1.72207 | 1.19456 |
| H | -0.38750 | 2.39620 | 2.17379 |
| C | -1.82885 | 3.74489 | -0.66618 |
| H | -1.45868 | 4.24667 | -1.56491 |
| H | -2.36376 | 2.84114 | -0.97298 |
| H | -2.53430 | 4.41293 | -0.16043 |
| H | 0.51035 | 0.34467 | -0.69942 |

**Prod: 21** + HOtBu in DMSO

42

-877.0023769

| | | | |
|---|---|---|---|
| C | 2.69497 | 2.61842 | 1.45047 |
| C | 1.59535 | 2.33744 | 0.64847 |
| C | 1.41930 | 1.07633 | 0.07229 |
| C | 2.39166 | 0.11060 | 0.33257 |
| C | 3.49981 | 0.37377 | 1.13030 |
| C | 3.64944 | 1.63700 | 1.69304 |
| H | 2.80501 | 3.60450 | 1.88555 |
| H | 0.84981 | 3.10397 | 0.46534 |
| H | 4.24035 | -0.39542 | 1.30995 |
| H | 4.51112 | 1.84716 | 2.31512 |
| C | 0.21502 | 0.78234 | -0.80575 |
| H | 0.55934 | 0.45459 | -1.78995 |
| H | -0.37621 | -0.03330 | -0.38554 |
| N | -0.63594 | 1.93814 | -1.00747 |
| C | -0.39087 | 2.82675 | -2.02396 |
| C | -1.68676 | 2.40442 | -0.23216 |
| C | -1.28454 | 3.86642 | -1.92658 |
| H | 0.39765 | 2.63214 | -2.73522 |
| C | -2.10494 | 3.59358 | -0.80267 |
| H | -2.92691 | 4.18288 | -0.42954 |
| H | -1.34532 | 4.71180 | -2.59444 |
| C | -2.31103 | 1.77948 | 0.98861 |
| C | -1.61702 | 0.86227 | 1.75074 |
| H | -0.56973 | 0.64252 | 1.60834 |
| H | -2.09552 | 0.47112 | 2.64256 |
| O | -3.50431 | 2.17508 | 1.22630 |
| I | 2.22546 | -1.84586 | -0.50579 |
| H | -2.71992 | -0.43731 | 0.36791 |
| O | -3.21196 | -1.01027 | -0.25067 |
| C | -3.05535 | -2.36573 | 0.17901 |
| C | -3.64270 | -2.52860 | 1.58092 |
| H | -3.10929 | -1.88889 | 2.28944 |
| H | -4.69790 | -2.24458 | 1.58163 |
| H | -3.55911 | -3.56420 | 1.92003 |
| C | -1.57124 | -2.72763 | 0.17605 |
| H | -1.41789 | -3.76683 | 0.47909 |
| H | -1.15260 | -2.59031 | -0.82435 |
| H | -1.02244 | -2.08268 | 0.86975 |
| C | -3.81920 | -3.21680 | -0.82625 |
| H | -4.87298 | -2.92810 | -0.84094 |
| H | -3.40554 | -3.07936 | -1.82814 |
| H | -3.75087 | -4.27472 | -0.56298 |




**9** **21**

**SM: 9** + tert-butoxide anion in Benzene

42

-876.9509341

| | | | |
|---|---|---|---|
| C | -1.10231 | -3.82205 | 0.25083 |
| C | -0.21375 | -2.82173 | -0.12513 |
| C | -0.61524 | -1.48569 | -0.22747 |
| C | -1.95551 | -1.20299 | 0.04581 |
| C | -2.85869 | -2.19145 | 0.41947 |
| C | -2.42781 | -3.50900 | 0.52824 |
| H | -0.75518 | -4.84565 | 0.32661 |
| H | 0.81922 | -3.07502 | -0.33994 |
| H | -3.89053 | -1.93537 | 0.62482 |
| H | -3.12840 | -4.28026 | 0.82533 |
| C | 0.35273 | -0.39263 | -0.62649 |
| H | 0.00096 | 0.06424 | -1.55600 |
| H | 0.42373 | 0.44398 | 0.09649 |
| N | 1.69184 | -0.89818 | -0.89973 |
| C | 2.09640 | -1.21187 | -2.15915 |
| C | 2.70092 | -1.23565 | -0.01233 |
| C | 3.37032 | -1.74510 | -2.11316 |
| H | 1.44354 | -1.01967 | -2.99701 |
| C | 3.74782 | -1.75987 | -0.75754 |
| H | 4.67743 | -2.10006 | -0.32963 |
| H | 3.95210 | -2.06650 | -2.96257 |
| C | 2.71881 | -1.12470 | 1.46642 |
| C | 1.54130 | -0.59176 | 2.22758 |
| H | 0.63217 | -1.14890 | 1.98868 |
| H | 1.75754 | -0.68551 | 3.29094 |
| O | 3.73328 | -1.47895 | 2.04677 |
| I | -2.69706 | 0.78751 | -0.13478 |
| H | 1.38278 | 0.46280 | 1.95147 |
| O | 1.07975 | 2.07440 | 0.91107 |
| C | 1.20306 | 3.19338 | 0.13683 |
| C | 2.62908 | 3.78259 | 0.23958 |
| H | 2.84379 | 4.02112 | 1.28573 |
| H | 3.35235 | 3.03068 | -0.09146 |
| H | 2.76209 | 4.68954 | -0.36355 |
| C | 0.20025 | 4.28569 | 0.57656 |
| H | 0.26969 | 5.20041 | -0.02545 |
| H | -0.81698 | 3.88878 | 0.49796 |
| H | 0.38451 | 4.53956 | 1.62497 |
| C | 0.93022 | 2.87568 | -1.35499 |
| H | 1.62096 | 2.09302 | -1.68938 |
| H | -0.09290 | 2.50061 | -1.46484 |
| H | 1.05236 | 3.75091 | -2.00471 |

**TS: 9** + tert-butoxide anion in Benzene

42

-876.9444239

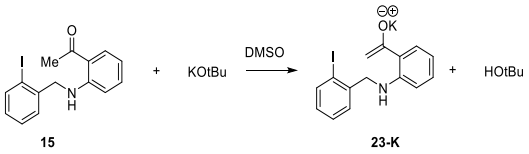
| | | | |
|---|---|---|---|
| C | 0.37815 | -2.71351 | 2.43847 |
| C | 0.92199 | -2.04338 | 1.35019 |
| C | 0.11263 | -1.42732 | 0.39103 |
| C | -1.26830 | -1.53039 | 0.56158 |
| C | -1.83088 | -2.19587 | 1.64548 |
| C | -1.00151 | -2.78669 | 2.59196 |
| H | 1.03468 | -3.17467 | 3.16663 |
| H | 1.99938 | -1.98414 | 1.23427 |
| H | -2.90695 | -2.25509 | 1.74856 |
| H | -1.43836 | -3.30248 | 3.43878 |
| C | 0.71976 | -0.67128 | -0.77407 |
| H | 0.25063 | -1.00774 | -1.70177 |
| N | 2.14971 | -0.90348 | -0.91506 |
| C | 2.62663 | -1.99403 | -1.58675 |
| C | 3.22024 | -0.16172 | -0.44676 |
| C | 4.00348 | -1.97282 | -1.55974 |
| H | 1.93843 | -2.69069 | -2.04140 |
| C | 4.37519 | -0.81062 | -0.84582 |
| H | 5.36872 | -0.45554 | -0.62293 |
| H | 4.65619 | -2.70314 | -2.01187 |
| C | 3.20220 | 1.07744 | 0.39526 |
| C | 2.01609 | 1.41632 | 1.16510 |
| H | 1.49449 | 0.55196 | 1.57785 |
| H | 2.25704 | 2.14717 | 1.93777 |
| O | 4.22458 | 1.76406 | 0.37494 |
| I | -2.61304 | -0.71389 | -0.88148 |
| H | 1.15950 | 1.96098 | 0.38952 |
| O | 0.16129 | 2.43707 | -0.43774 |
| C | -0.70095 | 3.28670 | 0.23773 |
| C | 0.03174 | 4.57926 | 0.64833 |
| H | 0.88339 | 4.33101 | 1.28834 |
| H | 0.41598 | 5.07784 | -0.24604 |
| H | -0.62095 | 5.27519 | 1.18757 |
| C | -1.25724 | 2.60891 | 1.50806 |
| H | -1.96461 | 3.25304 | 2.04266 |
| H | -1.76861 | 1.68132 | 1.23176 |
| H | -0.43840 | 2.35651 | 2.18820 |
| C | -1.87873 | 3.65279 | -0.67871 |
| H | -1.49635 | 4.11994 | -1.59066 |
| H | -2.41672 | 2.74317 | -0.96041 |
| H | -2.58010 | 4.34298 | -0.19540 |
| H | 0.50556 | 0.40098 | -0.68318 |

**Prod: 21** + HOtBu in Benzene

42

-876.9612529

| | | | |
|---|---|---|---|
| C | -2.03379 | -2.92336 | 1.78231 |
| C | -1.04666 | -2.58914 | 0.86355 |
| C | -1.10570 | -1.39774 | 0.13564 |
| C | -2.19105 | -0.55575 | 0.37328 |
| C | -3.18914 | -0.87298 | 1.28728 |
| C | -3.10823 | -2.06698 | 1.99517 |
| H | -1.95862 | -3.85176 | 2.33574 |
| H | -0.20019 | -3.24948 | 0.70726 |
| H | -4.01766 | -0.19495 | 1.44804 |
| H | -3.88202 | -2.31763 | 2.71110 |
| C | -0.02566 | -1.03867 | -0.86766 |
| H | -0.48026 | -0.94134 | -1.85823 |
| H | 0.40791 | -0.06894 | -0.62127 |
| N | 1.02404 | -2.02983 | -0.96392 |
| C | 0.91957 | -3.10630 | -1.81107 |
| C | 2.21235 | -2.11285 | -0.25679 |
| C | 2.03976 | -3.88889 | -1.66305 |
| H | 0.05850 | -3.20748 | -2.45431 |
| C | 2.85619 | -3.25547 | -0.69134 |
| H | 3.82397 | -3.56540 | -0.33113 |
| H | 2.24996 | -4.79821 | -2.20503 |
| C | 2.75937 | -1.16867 | 0.79123 |
| C | 1.88534 | -0.41997 | 1.56469 |
| H | 0.81808 | -0.59305 | 1.57344 |
| H | 2.30729 | 0.16562 | 2.37514 |
| O | 4.02199 | -1.16099 | 0.88040 |
| I | -2.37679 | 1.29402 | -0.67959 |
| H | 1.92454 | 1.12316 | 0.18165 |
| O | 1.80123 | 1.86799 | -0.44849 |
| C | 2.08156 | 3.07913 | 0.24302 |
| C | 3.52418 | 3.05371 | 0.75056 |
| H | 3.66834 | 2.20857 | 1.42930 |
| H | 4.21246 | 2.93453 | -0.08935 |
| H | 3.77054 | 3.97743 | 1.28195 |
| C | 1.10683 | 3.24715 | 1.41182 |
| H | 1.28293 | 4.19197 | 1.93431 |
| H | 0.07815 | 3.23372 | 1.04297 |
| H | 1.22657 | 2.42660 | 2.12371 |
| C | 1.88533 | 4.19736 | -0.77356 |
| H | 2.56896 | 4.06158 | -1.61481 |
| H | 0.86026 | 4.17844 | -1.15252 |
| H | 2.07474 | 5.17295 | -0.31827 |




15 23-K

**SM: 15** + KOtBu in DMSO
47
-1554.2949997

| | | | |
|---|---|---|---|
| C | 3.91388 | 3.35180 | 0.50774 |
| C | 2.97954 | 2.61965 | 1.23172 |
| C | 2.72040 | 1.27894 | 0.93921 |
| C | 3.43083 | 0.69585 | -0.11408 |
| C | 4.36763 | 1.41256 | -0.84878 |
| C | 4.60691 | 2.74733 | -0.53407 |
| H | 4.09731 | 4.39004 | 0.75591 |
| H | 2.43455 | 3.08937 | 2.04340 |
| H | 4.90807 | 0.93877 | -1.65815 |
| H | 5.33712 | 3.30654 | -1.10644 |
| C | 1.68158 | 0.52145 | 1.72613 |
| H | 2.09591 | -0.44068 | 2.04789 |
| H | 1.41601 | 1.08735 | 2.62229 |
| C | -0.31583 | -0.78594 | 1.07688 |
| C | -1.15982 | -1.28451 | 0.04281 |
| C | -0.34266 | -1.42944 | 2.32987 |
| C | -1.96098 | -2.40757 | 0.30421 |
| C | -1.15743 | -2.52469 | 2.55164 |
| H | 0.27045 | -1.05155 | 3.13739 |
| C | -1.97366 | -3.03000 | 1.53792 |
| H | -2.59516 | -2.79534 | -0.48273 |
| H | -1.15694 | -2.99118 | 3.53023 |
| H | -2.60744 | -3.88926 | 1.71410 |
| N | 0.50398 | 0.30294 | 0.88701 |
| O | -0.68897 | 0.43881 | -1.50734 |
| C | -1.21885 | -0.64798 | -1.29175 |
| C | -1.95132 | -1.34511 | -2.41048 |
| H | -3.02067 | -1.38970 | -2.18984 |
| H | -1.80094 | -0.77898 | -3.32700 |
| H | -1.59132 | -2.36718 | -2.53973 |
| I | 3.12844 | -1.35401 | -0.63877 |
| O | -3.96974 | 1.29283 | -0.14272 |
| C | -5.24583 | 0.81507 | -0.34103 |
| C | -6.27438 | 1.64004 | 0.46209 |
| H | -6.22797 | 2.68850 | 0.15093 |
| H | -7.30028 | 1.28204 | 0.32211 |
| H | -6.03410 | 1.58993 | 1.52876 |
| C | -5.36141 | -0.65607 | 0.11055 |
| H | -4.67106 | -1.27599 | -0.46993 |
| H | -5.08255 | -0.73967 | 1.16588 |
| H | -6.37296 | -1.05756 | -0.01497 |
| C | -5.63703 | 0.88842 | -1.83169 |
| H | -6.64792 | 0.50963 | -2.01925 |
| H | -5.58704 | 1.92677 | -2.17362 |
| H | -4.93217 | 0.29955 | -2.42723 |
| K | -1.80057 | 2.19550 | 0.40117 |
| H | 0.60482 | 0.58424 | -0.07974 |

**TS: 15** + KOtBu in DMSO
47
-1554.2868368

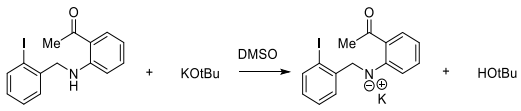
| | | | |
|---|---|---|---|
| C | -2.02918 | 3.29105 | -1.27630 |
| C | -1.33430 | 2.15277 | -1.66722 |
| C | -1.70160 | 0.87993 | -1.21723 |
| C | -2.79567 | 0.79248 | -0.35338 |
| C | -3.50440 | 1.92086 | 0.04729 |
| C | -3.11579 | 3.17353 | -0.41623 |
| H | -1.72281 | 4.26352 | -1.64168 |
| H | -0.48319 | 2.23971 | -2.33474 |
| H | -4.35032 | 1.82768 | 0.71600 |
| H | -3.66818 | 4.05173 | -0.10432 |
| C | -0.86424 | -0.30993 | -1.61542 |
| H | -1.50036 | -1.16040 | -1.89490 |
| H | -0.26917 | -0.03903 | -2.49047 |
| C | 0.98695 | -1.63477 | -0.64946 |
| C | 1.83599 | -1.95162 | 0.44161 |
| C | 1.17825 | -2.30569 | -1.86631 |
| C | 2.79590 | -2.95148 | 0.28952 |
| C | 2.15137 | -3.29090 | -1.99041 |
| H | 0.55451 | -2.07270 | -2.71941 |
| C | 2.95577 | -3.63629 | -0.90992 |
| H | 3.42960 | -3.19962 | 1.13308 |
| H | 2.26814 | -3.79902 | -2.94096 |
| H | 3.70140 | -4.41592 | -1.00226 |
| N | 0.03720 | -0.62734 | -0.51802 |
| O | 0.64944 | -0.76324 | 2.11678 |
| C | 1.75814 | -1.16720 | 1.71860 |
| C | 2.99646 | -0.73413 | 2.32158 |
| H | 3.11645 | 0.35986 | 1.66441 |
| H | 2.89173 | -0.45635 | 3.36948 |
| H | 3.87802 | -1.33225 | 2.11029 |
| I | -3.44912 | -1.09565 | 0.40319 |
| O | 3.03161 | 1.58917 | 1.02367 |
| C | 3.66261 | 1.72263 | -0.21718 |
| C | 2.60411 | 1.97613 | -1.30519 |
| H | 2.05083 | 2.89535 | -1.08106 |
| H | 3.05002 | 2.08480 | -2.29907 |
| H | 1.89661 | 1.13948 | -1.32814 |
| C | 4.44581 | 0.45016 | -0.58300 |
| H | 5.18689 | 0.22918 | 0.19136 |
| H | 3.76777 | -0.40480 | -0.66233 |
| H | 4.96783 | 0.56874 | -1.53733 |
| C | 4.63578 | 2.91033 | -0.17934 |
| H | 5.12998 | 3.06526 | -1.14392 |
| H | 4.09388 | 3.82324 | 0.08384 |
| H | 5.40367 | 2.73653 | 0.58006 |
| K | 0.53243 | 1.91320 | 1.40163 |
| H | -0.38662 | -0.62945 | 0.40253 |

**Prod: 23-K** + HOtBu in DMSO

47

-1554.3089965

| | | | |
|---|---|---|---|
| C | 4.29776 | 3.05512 | 0.63285 |
| C | 3.38922 | 2.31982 | 1.38589 |
| C | 2.93936 | 1.06537 | 0.96785 |
| C | 3.43458 | 0.57324 | -0.24383 |
| C | 4.34357 | 1.29305 | -1.00994 |
| C | 4.77410 | 2.54108 | -0.56718 |
| H | 4.63082 | 4.02472 | 0.98243 |
| H | 3.01399 | 2.71851 | 2.32240 |
| H | 4.71738 | 0.88889 | -1.94214 |
| H | 5.48229 | 3.10288 | -1.16423 |
| C | 1.93567 | 0.31017 | 1.80240 |
| H | 2.28451 | -0.71992 | 1.95098 |
| H | 1.87084 | 0.77645 | 2.78988 |
| C | -0.24099 | -0.74843 | 1.31156 |
| C | -1.16979 | -1.11459 | 0.30026 |
| C | -0.23044 | -1.46191 | 2.52373 |
| C | -2.06879 | -2.14751 | 0.58391 |
| C | -1.12421 | -2.49721 | 2.75719 |
| H | 0.47480 | -1.18250 | 3.29728 |
| C | -2.05963 | -2.84313 | 1.78698 |
| H | -2.80541 | -2.40707 | -0.16622 |
| H | -1.09591 | -3.02231 | 3.70533 |
| H | -2.77629 | -3.63572 | 1.96475 |
| N | 0.63761 | 0.31316 | 1.13725 |
| O | -0.76811 | 0.81175 | -1.06755 |
| C | -1.20188 | -0.40975 | -1.04295 |
| C | -1.72727 | -1.05786 | -2.13021 |
| H | -3.28447 | 0.41748 | -1.21294 |
| H | -1.74690 | -0.54425 | -3.08489 |
| H | -2.04046 | -2.09154 | -2.09917 |
| I | 2.83385 | -1.34513 | -0.96702 |
| O | -3.76279 | 1.08088 | -0.68527 |
| C | -5.16055 | 0.75762 | -0.68549 |
| C | -5.81260 | 1.74890 | 0.26806 |
| H | -5.63428 | 2.77191 | -0.07156 |
| H | -6.89029 | 1.58030 | 0.31589 |
| H | -5.39798 | 1.63525 | 1.27284 |
| C | -5.34883 | -0.67579 | -0.19443 |
| H | -4.86748 | -1.37773 | -0.88215 |
| H | -4.90227 | -0.79898 | 0.79542 |
| H | -6.41063 | -0.92696 | -0.13664 |
| C | -5.71151 | 0.91714 | -2.10071 |
| H | -6.77892 | 0.68521 | -2.12890 |
| H | -5.56609 | 1.94186 | -2.44968 |
| H | -5.19478 | 0.23894 | -2.78618 |
| K | -1.87620 | 2.07629 | 0.93561 |
| H | 0.60854 | 0.68182 | 0.18896 |




15 24-K

**SM: 15** + KOtBu in DMSO

47

-1554.2992212

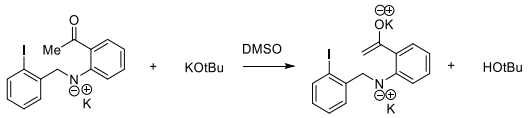
| | | | |
|---|---|---|---|
| C | -2.35842 | 3.31462 | -0.94803 |
| C | -1.47120 | 2.40986 | -1.51980 |
| C | -1.49637 | 1.05162 | -1.19611 |
| C | -2.45525 | 0.63180 | -0.26815 |
| C | -3.35693 | 1.51797 | 0.30833 |
| C | -3.30295 | 2.86723 | -0.03208 |
| H | -2.31189 | 4.36329 | -1.21607 |
| H | -0.73190 | 2.75059 | -2.23592 |
| H | -4.10046 | 1.16613 | 1.01211 |
| H | -4.00248 | 3.55980 | 0.42061 |
| C | -0.50984 | 0.11051 | -1.84636 |
| H | -1.04992 | -0.77094 | -2.19457 |
| H | -0.07035 | 0.59816 | -2.72492 |
| C | 1.04946 | -1.51602 | -0.80106 |
| C | 1.78907 | -1.96398 | 0.33879 |
| C | 0.93381 | -2.41472 | -1.89466 |
| C | 2.41191 | -3.22417 | 0.29735 |
| C | 1.53558 | -3.65994 | -1.87962 |
| H | 0.40080 | -2.11478 | -2.78552 |
| C | 2.29976 | -4.07657 | -0.78680 |
| H | 2.98405 | -3.55164 | 1.15646 |
| H | 1.42064 | -4.30678 | -2.74297 |
| H | 2.78626 | -5.04354 | -0.78227 |
| N | 0.49475 | -0.27324 | -0.87275 |
| O | 1.03395 | -0.27656 | 1.78746 |
| C | 1.79259 | -1.21504 | 1.61768 |
| C | 2.72256 | -1.63696 | 2.73401 |
| H | 3.74647 | -1.74494 | 2.37149 |
| H | 2.68373 | -0.87852 | 3.51343 |
| H | 2.41288 | -2.59505 | 3.15625 |
| I | -2.60254 | -1.42457 | 0.28767 |
| O | 1.64282 | 2.14846 | 0.14657 |
| C | 2.84258 | 2.24525 | -0.53080 |
| C | 3.83412 | 1.15458 | -0.07063 |
| H | 3.41499 | 0.16098 | -0.25988 |
| H | 4.79639 | 1.22165 | -0.59112 |
| H | 4.01690 | 1.25119 | 1.00407 |
| C | 3.49805 | 3.61838 | -0.27400 |
| H | 2.82802 | 4.41371 | -0.61482 |
| H | 3.66297 | 3.74930 | 0.80047 |
| H | 4.45866 | 3.73394 | -0.78829 |
| C | 2.65296 | 2.10301 | -2.05485 |
| H | 3.59870 | 2.19757 | -2.60067 |
| H | 2.21924 | 1.12662 | -2.28847 |
| H | 1.97158 | 2.88014 | -2.41538 |
| K | 0.13962 | 2.20468 | 2.06791 |
| H | 0.79982 | 0.47952 | -0.25357 |

**Prod: 24-K** + HOtBu in DMSO

47

-1554.3150774

| | | | |
|---|---|---|---|
| C | -2.38203 | 3.25098 | -0.71370 |
| C | -1.45383 | 2.34733 | -1.22003 |
| C | -1.58176 | 0.96837 | -1.02258 |
| C | -2.68969 | 0.53173 | -0.29061 |
| C | -3.63442 | 1.41789 | 0.21995 |
| C | -3.47518 | 2.78485 | 0.00881 |
| H | -2.25083 | 4.31305 | -0.88139 |
| H | -0.59622 | 2.70865 | -1.77683 |
| H | -4.48442 | 1.05001 | 0.78035 |
| H | -4.20717 | 3.47541 | 0.40955 |
| C | -0.50363 | 0.03558 | -1.52001 |
| H | -0.98710 | -0.85163 | -1.95050 |
| H | 0.02937 | 0.53229 | -2.34622 |
| C | 1.28738 | -1.25054 | -0.65810 |
| C | 2.24825 | -1.67387 | 0.34960 |
| C | 1.42729 | -1.88938 | -1.94529 |
| C | 3.24618 | -2.61009 | 0.00780 |
| C | 2.41122 | -2.80970 | -2.21670 |
| H | 0.74774 | -1.62311 | -2.74287 |
| C | 3.34912 | -3.18665 | -1.24076 |
| H | 3.96138 | -2.90812 | 0.76419 |
| H | 2.46388 | -3.24428 | -3.21029 |
| H | 4.12496 | -3.90915 | -1.45842 |
| N | 0.38319 | -0.29911 | -0.41573 |
| O | 1.29328 | -0.55403 | 2.22418 |
| C | 2.22327 | -1.19319 | 1.73421 |
| C | 3.40382 | -1.50364 | 2.64424 |
| H | 4.35306 | -1.22704 | 2.18238 |
| H | 3.27104 | -0.94420 | 3.56802 |
| H | 3.44452 | -2.56900 | 2.88289 |
| I | -2.98888 | -1.54583 | 0.10885 |
| O | 1.70880 | 1.96947 | 0.39344 |
| C | 2.85447 | 2.33716 | -0.37635 |
| C | 4.07233 | 1.56642 | 0.13729 |
| H | 3.92094 | 0.49146 | 0.00166 |
| H | 4.97732 | 1.86071 | -0.40069 |
| H | 4.21836 | 1.76557 | 1.20213 |
| C | 3.04563 | 3.83563 | -0.17674 |
| H | 2.16683 | 4.37769 | -0.53458 |
| H | 3.18471 | 4.05886 | 0.88392 |
| H | 3.92238 | 4.18938 | -0.72392 |
| C | 2.61437 | 2.01545 | -1.85159 |
| H | 3.48089 | 2.30253 | -2.45218 |
| H | 2.44241 | 0.94250 | -1.98589 |
| H | 1.74206 | 2.55900 | -2.22335 |
| K | -0.43918 | 1.28436 | 1.83829 |
| H | 1.35294 | 1.09960 | 0.06788 |




24-K 25-K

**SM: 24-K** + KOtBu in DMSO

46

-1553.7986697

| | | | |
|---|---|---|---|
| C | -1.90090 | -3.10103 | 1.75851 |
| C | -1.32907 | -1.86459 | 2.03750 |
| C | -1.69608 | -0.70591 | 1.34406 |
| C | -2.67104 | -0.84413 | 0.35351 |
| C | -3.26125 | -2.07056 | 0.06012 |
| C | -2.86972 | -3.20457 | 0.76601 |
| H | -1.58886 | -3.97909 | 2.31092 |
| H | -0.56534 | -1.78348 | 2.80406 |
| H | -4.01450 | -2.14550 | -0.71379 |
| H | -3.32471 | -4.16030 | 0.53579 |
| C | -0.96959 | 0.58773 | 1.62705 |
| H | -1.70363 | 1.40804 | 1.65297 |
| H | -0.54829 | 0.51823 | 2.64161 |
| C | 0.80656 | 1.86861 | 0.76543 |
| C | 1.91186 | 2.18669 | -0.13909 |
| C | 0.62497 | 2.81476 | 1.85301 |
| C | 2.75392 | 3.28190 | 0.15016 |
| C | 1.46398 | 3.87844 | 2.06629 |
| H | -0.20198 | 2.67633 | 2.53589 |
| C | 2.56488 | 4.12695 | 1.22318 |
| H | 3.58357 | 3.48739 | -0.51516 |
| H | 1.27065 | 4.53978 | 2.90598 |
| H | 3.22911 | 4.96311 | 1.39951 |
| N | 0.05662 | 0.78905 | 0.61768 |
| O | 1.40827 | 0.61489 | -1.85553 |
| C | 2.18202 | 1.43864 | -1.36343 |
| C | 3.49145 | 1.67974 | -2.10741 |
| H | 4.35457 | 1.58441 | -1.44559 |
| H | 3.56289 | 0.94168 | -2.90400 |
| H | 3.51666 | 2.67775 | -2.55116 |
| I | -3.30430 | 0.83763 | -0.80214 |
| O | 2.08681 | -2.63846 | 0.15913 |
| C | 3.43968 | -2.41210 | 0.04039 |
| C | 4.25555 | -3.60753 | 0.57669 |
| H | 3.98486 | -4.51251 | 0.02346 |
| H | 5.33711 | -3.45621 | 0.48588 |
| H | 4.01627 | -3.77046 | 1.63250 |
| C | 3.86085 | -1.15223 | 0.82956 |
| H | 3.31967 | -0.27963 | 0.44753 |
| H | 3.59947 | -1.27825 | 1.88547 |
| H | 4.93609 | -0.94997 | 0.76026 |
| C | 3.82453 | -2.19090 | -1.43987 |
| H | 4.89368 | -1.98998 | -1.57547 |
| H | 3.56299 | -3.08045 | -2.02275 |
| H | 3.25838 | -1.34145 | -1.83563 |
| K | 0.17877 | -1.47673 | -1.00567 |

**TS: 24-K** + KOtBu in DMSO

46

-1553.7834681

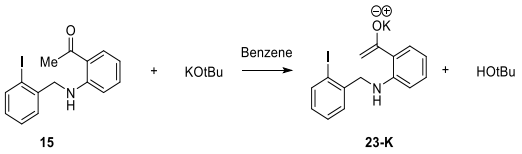
| | | | |
|---|---|---|---|
| C | 2.01200 | 3.34716 | 1.25476 |
| C | 1.30254 | 2.23252 | 1.69032 |
| C | 1.58965 | 0.94397 | 1.22731 |
| C | 2.63754 | 0.82427 | 0.31100 |
| C | 3.36252 | 1.92361 | -0.13846 |
| C | 3.04129 | 3.19361 | 0.33292 |
| H | 1.75854 | 4.33096 | 1.63147 |
| H | 0.49388 | 2.35428 | 2.40305 |
| H | 4.16840 | 1.79566 | -0.85014 |
| H | 3.60102 | 4.05208 | -0.01872 |
| C | 0.72048 | -0.22199 | 1.64087 |
| H | 1.37342 | -1.06159 | 1.93806 |
| H | 0.17028 | 0.06902 | 2.55346 |
| C | -0.94333 | -1.61227 | 0.71857 |
| C | -1.89185 | -2.00449 | -0.30719 |
| C | -0.97837 | -2.41792 | 1.91022 |
| C | -2.78179 | -3.04819 | -0.09375 |
| C | -1.86457 | -3.47388 | 2.06967 |
| H | -0.29907 | -2.19097 | 2.72258 |
| C | -2.78534 | -3.81163 | 1.07841 |
| H | -3.48860 | -3.28723 | -0.88377 |
| H | -1.83895 | -4.04218 | 2.99561 |
| H | -3.47946 | -4.63253 | 1.20764 |
| N | -0.15529 | -0.55159 | 0.54004 |
| O | -0.91416 | -1.13411 | -2.30320 |
| C | -1.95082 | -1.30305 | -1.63307 |
| C | -3.21891 | -0.73702 | -2.03910 |
| H | -3.09260 | 0.47301 | -1.53161 |
| H | -3.30888 | -0.59344 | -3.11689 |
| H | -4.10293 | -1.17216 | -1.57937 |
| I | 3.22212 | -1.09073 | -0.43651 |
| O | -2.84329 | 1.72199 | -1.12512 |
| C | -3.36095 | 2.07335 | 0.12794 |
| C | -2.20998 | 2.47910 | 1.06287 |
| H | -1.63454 | 3.29595 | 0.61272 |
| H | -2.57282 | 2.81645 | 2.03959 |
| H | -1.54365 | 1.62345 | 1.21442 |
| C | -4.11196 | 0.89268 | 0.76983 |
| H | -4.96008 | 0.59466 | 0.14606 |
| H | -3.44401 | 0.03048 | 0.86971 |
| H | -4.49055 | 1.16245 | 1.76059 |
| C | -4.32754 | 3.25687 | -0.02225 |
| H | -4.74368 | 3.56997 | 0.94102 |
| H | -3.80435 | 4.10882 | -0.46651 |
| H | -5.15394 | 2.97991 | -0.68324 |
| K | -0.24616 | 1.34049 | -1.41526 |

**Prod: 25-K** + HOtBu in DMSO

46

-1553.8064365

| | | | |
|---|---|---|---|
| C | -1.53869 | 3.50990 | -0.75777 |
| C | -0.87616 | 2.39790 | -1.26554 |
| C | -1.34920 | 1.09574 | -1.06748 |
| C | -2.52960 | 0.96129 | -0.33448 |
| C | -3.21482 | 2.05878 | 0.18004 |
| C | -2.71190 | 3.33947 | -0.03023 |
| H | -1.13922 | 4.50298 | -0.92690 |
| H | 0.04335 | 2.52492 | -1.82814 |
| H | -4.13089 | 1.91983 | 0.74043 |
| H | -3.24103 | 4.19432 | 0.37347 |
| C | -0.51664 | -0.07341 | -1.53971 |
| H | -1.17975 | -0.83002 | -1.99812 |
| H | 0.13195 | 0.28643 | -2.35915 |
| C | 1.05948 | -1.59468 | -0.67700 |
| C | 1.82967 | -2.16874 | 0.40309 |
| C | 1.26077 | -2.19304 | -1.96159 |
| C | 2.69038 | -3.22575 | 0.17830 |
| C | 2.14799 | -3.25155 | -2.15306 |
| H | 0.71457 | -1.81655 | -2.81852 |
| C | 2.87635 | -3.78829 | -1.09814 |
| H | 3.24348 | -3.62702 | 1.02438 |
| H | 2.26441 | -3.66301 | -3.15234 |
| H | 3.56211 | -4.61343 | -1.24811 |
| N | 0.22732 | -0.57857 | -0.41289 |
| O | 2.36724 | -0.46520 | 2.00329 |
| C | 1.71810 | -1.57564 | 1.78460 |
| C | 0.94492 | -2.20483 | 2.71665 |
| H | 2.57552 | 0.92929 | 1.14238 |
| H | 0.85600 | -1.80068 | 3.72122 |
| H | 0.41867 | -3.12025 | 2.47727 |
| I | -3.37734 | -0.96710 | 0.03410 |
| O | 2.51662 | 1.88062 | 0.86238 |
| C | 3.41816 | 2.10255 | -0.21978 |
| C | 3.14798 | 3.51291 | -0.72892 |
| H | 3.31310 | 4.24198 | 0.06840 |
| H | 3.80860 | 3.75571 | -1.56460 |
| H | 2.11261 | 3.59927 | -1.06770 |
| C | 3.16662 | 1.07117 | -1.31976 |
| H | 3.28682 | 0.05861 | -0.92347 |
| H | 2.14268 | 1.15339 | -1.69180 |
| H | 3.86369 | 1.21523 | -2.14991 |
| C | 4.85705 | 1.98852 | 0.28919 |
| H | 5.57348 | 2.17065 | -0.51611 |
| H | 5.03315 | 2.71699 | 1.08459 |
| H | 5.03698 | 0.98682 | 0.68967 |
| K | 0.09283 | 0.91702 | 1.82580 |




15 23-K

**SM: 15** + KOtBu in Benzene
47
-1554.2794231

| | | | |
|---|---|---|---|
| C | 4.22831 | 3.14552 | 0.53793 |
| C | 3.24955 | 2.47523 | 1.26202 |
| C | 2.86445 | 1.17351 | 0.93615 |
| C | 3.49527 | 0.56271 | -0.15215 |
| C | 4.47592 | 1.21825 | -0.88678 |
| C | 4.84137 | 2.51499 | -0.53775 |
| H | 4.51068 | 4.15413 | 0.81388 |
| H | 2.76953 | 2.96309 | 2.10365 |
| H | 4.95571 | 0.72388 | -1.72183 |
| H | 5.60776 | 3.02453 | -1.10929 |
| C | 1.79061 | 0.48230 | 1.73633 |
| H | 2.12994 | -0.52449 | 2.00675 |
| H | 1.61821 | 1.03397 | 2.66444 |
| C | -0.33618 | -0.63248 | 1.16920 |
| C | -1.24043 | -1.07236 | 0.16421 |
| C | -0.38350 | -1.25198 | 2.43139 |
| C | -2.14253 | -2.09927 | 0.47073 |
| C | -1.28904 | -2.26497 | 2.69632 |
| H | 0.28567 | -0.92101 | 3.21500 |
| C | -2.17956 | -2.69927 | 1.71595 |
| H | -2.84686 | -2.41716 | -0.28620 |
| H | -1.30325 | -2.71558 | 3.68226 |
| H | -2.89508 | -3.48391 | 1.92513 |
| N | 0.55901 | 0.40301 | 0.95051 |
| O | -0.61940 | 0.54424 | -1.44685 |
| C | -1.26852 | -0.46688 | -1.19179 |
| C | -2.11536 | -1.09274 | -2.26304 |
| H | -3.15537 | -0.87787 | -2.00230 |
| H | -1.87716 | -0.61586 | -3.21150 |
| H | -1.96493 | -2.17062 | -2.33268 |
| I | 2.99766 | -1.43326 | -0.72066 |
| O | -3.76678 | 0.96203 | -0.37343 |
| C | -5.11698 | 0.71673 | -0.44393 |
| C | -5.88860 | 1.62583 | 0.53757 |
| H | -5.68154 | 2.67414 | 0.29918 |
| H | -6.97247 | 1.46933 | 0.50043 |
| H | -5.54568 | 1.43180 | 1.55900 |
| C | -5.43921 | -0.74937 | -0.08114 |
| H | -4.97874 | -1.42689 | -0.80742 |
| H | -5.02770 | -0.97926 | 0.90642 |
| H | -6.51649 | -0.94902 | -0.06970 |
| C | -5.64973 | 0.98842 | -1.86688 |
| H | -6.72496 | 0.79879 | -1.95976 |
| H | -5.45456 | 2.03116 | -2.13477 |
| H | -5.12283 | 0.35176 | -2.58449 |
| K | -1.87094 | 2.18067 | 0.38270 |
| H | 0.66313 | 0.63887 | -0.02958 |

**TS: 15** + KOtBu in Benzene
47
-1554.2703528

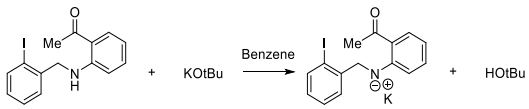
| | | | |
|---|---|---|---|
| C | 4.95770 | -2.15027 | -1.65735 |
| C | 4.18278 | -1.07006 | -2.06384 |
| C | 3.46427 | -0.29950 | -1.14752 |
| C | 3.54455 | -0.65720 | 0.20173 |
| C | 4.31576 | -1.73290 | 0.62575 |
| C | 5.02357 | -2.48160 | -0.30993 |
| H | 5.50564 | -2.72932 | -2.39067 |
| H | 4.12721 | -0.80911 | -3.11526 |
| H | 4.36734 | -1.98600 | 1.67708 |
| H | 5.62430 | -3.32018 | 0.02147 |
| C | 2.62494 | 0.85654 | -1.63316 |
| H | 2.87541 | 1.75489 | -1.05546 |
| H | 2.87306 | 1.06103 | -2.67986 |
| C | 0.29198 | 1.53170 | -1.19293 |
| C | -0.88498 | 1.26590 | -0.44156 |
| C | 0.51542 | 2.84721 | -1.64233 |
| C | -1.79983 | 2.30310 | -0.22957 |
| C | -0.40752 | 3.85197 | -1.40497 |
| H | 1.40987 | 3.06787 | -2.21201 |
| C | -1.58484 | 3.58603 | -0.70797 |
| H | -2.71021 | 2.08548 | 0.31532 |
| H | -0.21140 | 4.84993 | -1.78098 |
| H | -2.31751 | 4.36500 | -0.53948 |
| N | 1.21256 | 0.55030 | -1.47354 |
| O | -0.63612 | -1.08943 | -0.38970 |
| C | -1.14996 | -0.08068 | 0.14526 |
| C | -2.07540 | -0.22120 | 1.24806 |
| H | -3.18616 | -0.52999 | 0.64680 |
| H | -1.85338 | -1.11343 | 1.83365 |
| H | -2.21293 | 0.65846 | 1.87054 |
| I | 2.50447 | 0.45558 | 1.69593 |
| O | -4.21715 | -1.04503 | -0.07996 |
| C | -5.46187 | -0.56841 | 0.33781 |
| C | -6.53643 | -1.04509 | -0.64659 |
| H | -6.53871 | -2.13818 | -0.68915 |
| H | -7.53537 | -0.70791 | -0.35295 |
| H | -6.31913 | -0.66042 | -1.64689 |
| C | -5.45877 | 0.96834 | 0.37540 |
| H | -4.73946 | 1.32384 | 1.11932 |
| H | -5.16546 | 1.35979 | -0.60274 |
| H | -6.44286 | 1.37028 | 0.63475 |
| C | -5.78341 | -1.10466 | 1.74178 |
| H | -6.75054 | -0.74475 | 2.10666 |
| H | -5.80206 | -2.19800 | 1.72476 |
| H | -5.00775 | -0.78664 | 2.44461 |
| K | -2.63305 | -2.60659 | -1.13767 |
| H | 0.97130 | -0.36504 | -1.11474 |

**Prod: 23-K** + HOtBu in Benzene

47

-1554.2916430

| | | | |
|---|---|---|---|
| C | 4.43272 | 2.91107 | 0.74058 |
| C | 3.52967 | 2.15784 | 1.48174 |
| C | 3.00967 | 0.95528 | 0.99824 |
| C | 3.42638 | 0.53174 | -0.26776 |
| C | 4.33001 | 1.27185 | -1.02107 |
| C | 4.83287 | 2.46600 | -0.51327 |
| H | 4.82086 | 3.84001 | 1.14071 |
| H | 3.21469 | 2.50099 | 2.46152 |
| H | 4.64169 | 0.92229 | -1.99692 |
| H | 5.53607 | 3.04174 | -1.10302 |
| C | 2.01547 | 0.17862 | 1.82427 |
| H | 2.32163 | -0.87443 | 1.87070 |
| H | 2.02434 | 0.56657 | 2.84720 |
| C | -0.21498 | -0.77059 | 1.38081 |
| C | -1.15303 | -1.08727 | 0.36405 |
| C | -0.20767 | -1.52127 | 2.56817 |
| C | -2.07178 | -2.10953 | 0.62145 |
| C | -1.11895 | -2.54713 | 2.77578 |
| H | 0.51515 | -1.28508 | 3.34048 |
| C | -2.06783 | -2.84131 | 1.80244 |
| H | -2.81509 | -2.33124 | -0.13441 |
| H | -1.09225 | -3.10633 | 3.70413 |
| H | -2.79685 | -3.62696 | 1.95975 |
| N | 0.68152 | 0.29203 | 1.23674 |
| O | -0.75335 | 0.88997 | -0.92386 |
| C | -1.17968 | -0.33495 | -0.95445 |
| C | -1.70138 | -0.94160 | -2.06304 |
| H | -3.20049 | 0.55085 | -1.07477 |
| H | -1.69997 | -0.39788 | -3.00043 |
| H | -1.99705 | -1.98098 | -2.07091 |
| I | 2.69893 | -1.28974 | -1.10325 |
| O | -3.74455 | 1.11974 | -0.49928 |
| C | -5.12431 | 0.80324 | -0.72591 |
| C | -5.91500 | 1.67693 | 0.23735 |
| H | -5.71162 | 2.73273 | 0.04274 |
| H | -6.98654 | 1.50250 | 0.12020 |
| H | -5.63823 | 1.44823 | 1.26974 |
| C | -5.35673 | -0.67828 | -0.43736 |
| H | -4.75811 | -1.29066 | -1.11803 |
| H | -5.06424 | -0.91521 | 0.58864 |
| H | -6.40927 | -0.93817 | -0.57445 |
| C | -5.47631 | 1.12940 | -2.17577 |
| H | -6.52840 | 0.91490 | -2.37846 |
| H | -5.28600 | 2.18494 | -2.38168 |
| H | -4.86463 | 0.52748 | -2.85391 |
| K | -1.82312 | 2.00414 | 1.07549 |
| H | 0.64826 | 0.66924 | 0.28950 |




15 24-K

**SM: 15** + KOtBu in Benzene

47

-1554.2875083

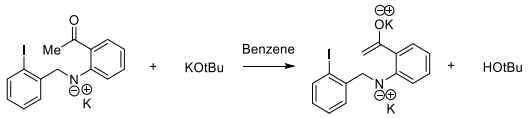
| | | | |
|---|---|---|---|
| C | 0.47626 | -3.96565 | -0.78078 |
| C | 0.09221 | -2.78397 | -1.39375 |
| C | 0.75918 | -1.57628 | -1.15254 |
| C | 1.82531 | -1.60367 | -0.25014 |
| C | 2.24091 | -2.78496 | 0.36246 |
| C | 1.55982 | -3.96755 | 0.09548 |
| H | -0.06084 | -4.88364 | -0.98213 |
| H | -0.74894 | -2.77043 | -2.07732 |
| H | 3.08825 | -2.78063 | 1.03709 |
| H | 1.87873 | -4.88627 | 0.57378 |
| C | 0.30858 | -0.30494 | -1.84114 |
| H | 1.20187 | 0.23171 | -2.16676 |
| H | -0.26854 | -0.55685 | -2.74035 |
| C | -0.25495 | 1.86090 | -0.80867 |
| C | -0.64490 | 2.60350 | 0.34247 |
| C | 0.32236 | 2.58185 | -1.87753 |
| C | -0.54192 | 4.00204 | 0.32953 |
| C | 0.44287 | 3.95492 | -1.83924 |
| H | 0.63635 | 2.05326 | -2.76895 |
| C | -0.00869 | 4.69289 | -0.73987 |
| H | -0.86765 | 4.55882 | 1.20031 |
| H | 0.87798 | 4.46121 | -2.69312 |
| H | 0.06463 | 5.77187 | -0.72015 |
| N | -0.44312 | 0.52376 | -0.92160 |
| O | -0.83360 | 0.72991 | 1.76363 |
| C | -1.02573 | 1.92171 | 1.60141 |
| C | -1.63971 | 2.73583 | 2.71896 |
| H | -2.50521 | 3.29382 | 2.35547 |
| H | -1.94720 | 2.05319 | 3.50837 |
| H | -0.92196 | 3.45298 | 3.12287 |
| I | 2.88913 | 0.18466 | 0.22879 |
| O | -2.39640 | -1.35736 | 0.14943 |
| C | -3.54574 | -0.93927 | -0.48373 |
| C | -3.88154 | 0.51767 | -0.10255 |
| H | -3.08511 | 1.19213 | -0.43263 |
| H | -4.81891 | 0.85623 | -0.55968 |
| H | -3.97452 | 0.59980 | 0.98499 |
| C | -4.73441 | -1.83001 | -0.06627 |
| H | -4.51949 | -2.86993 | -0.33082 |
| H | -4.87147 | -1.77688 | 1.01820 |
| H | -5.67333 | -1.53548 | -0.54925 |
| C | -3.39939 | -1.01598 | -2.01481 |
| H | -4.32752 | -0.72675 | -2.52071 |
| H | -2.60222 | -0.35095 | -2.35295 |
| H | -3.15182 | -2.03972 | -2.31094 |
| K | -0.87580 | -1.91387 | 1.90105 |
| H | -1.04800 | -0.01190 | -0.29046 |

**Prod: 24-K** + HOtBu in Benzene

47

-1554.3041079

| | | | |
|---|---|---|---|
| C | -2.49721 | 3.21857 | -0.66858 |
| C | -1.53408 | 2.37104 | -1.20586 |
| C | -1.59001 | 0.98514 | -1.02804 |
| C | -2.66002 | 0.48078 | -0.28252 |
| C | -3.63779 | 1.31132 | 0.25928 |
| C | -3.55170 | 2.68756 | 0.06636 |
| H | -2.42281 | 4.28845 | -0.82210 |
| H | -0.69956 | 2.78257 | -1.76304 |
| H | -4.45929 | 0.89030 | 0.82558 |
| H | -4.31133 | 3.33532 | 0.48741 |
| C | -0.47696 | 0.10879 | -1.55298 |
| H | -0.93126 | -0.77394 | -2.02351 |
| H | 0.04790 | 0.65639 | -2.35227 |
| C | 1.30811 | -1.19811 | -0.70561 |
| C | 2.22941 | -1.68829 | 0.30772 |
| C | 1.46523 | -1.78811 | -2.01247 |
| C | 3.19210 | -2.65924 | -0.04303 |
| C | 2.41815 | -2.73595 | -2.29403 |
| H | 0.82458 | -1.46126 | -2.81922 |
| C | 3.30664 | -3.19264 | -1.30728 |
| H | 3.87522 | -3.01369 | 0.71796 |
| H | 2.48516 | -3.12993 | -3.30346 |
| H | 4.05797 | -3.93879 | -1.53033 |
| N | 0.40559 | -0.24485 | -0.45077 |
| O | 1.37227 | -0.46036 | 2.16105 |
| C | 2.20458 | -1.24088 | 1.69999 |
| C | 3.26635 | -1.75330 | 2.66478 |
| H | 4.27167 | -1.51715 | 2.30960 |
| H | 3.10150 | -1.27127 | 3.62606 |
| H | 3.20119 | -2.83573 | 2.79256 |
| I | -2.83116 | -1.61094 | 0.10312 |
| O | 1.46904 | 2.15535 | 0.27408 |
| C | 2.72697 | 2.49764 | -0.30495 |
| C | 3.83391 | 1.67954 | 0.36119 |
| H | 3.67608 | 0.61303 | 0.17561 |
| H | 4.81535 | 1.95721 | -0.03237 |
| H | 3.82642 | 1.84995 | 1.44073 |
| C | 2.92597 | 3.98563 | -0.04793 |
| H | 2.11901 | 4.55771 | -0.51245 |
| H | 2.91947 | 4.18435 | 1.02652 |
| H | 3.87898 | 4.32660 | -0.45905 |
| C | 2.68601 | 2.20570 | -1.80590 |
| H | 3.63078 | 2.47915 | -2.28237 |
| H | 2.50951 | 1.13896 | -1.98043 |
| H | 1.88078 | 2.77453 | -2.27891 |
| K | -0.45994 | 1.19800 | 1.80905 |
| H | 1.22957 | 1.22809 | -0.00611 |




**24a** **25-K**

**SM: 24-K** + KOtBu in Benzene

46

-1553.7622425

| | | | |
|---|---|---|---|
| C | 2.51904 | -1.59834 | 1.98410 |
| C | 1.23925 | -1.12616 | 2.25128 |
| C | 0.16149 | -1.38724 | 1.39905 |
| C | 0.42507 | -2.15468 | 0.26251 |
| C | 1.69665 | -2.64244 | -0.02243 |
| C | 2.74845 | -2.35726 | 0.84301 |
| H | 3.33837 | -1.35395 | 2.64889 |
| H | 1.05915 | -0.51806 | 3.13191 |
| H | 1.87010 | -3.22884 | -0.91590 |
| H | 3.74356 | -2.71783 | 0.61233 |
| C | -1.18785 | -0.77143 | 1.68231 |
| H | -1.95609 | -1.54973 | 1.54910 |
| H | -1.21228 | -0.48947 | 2.74692 |
| C | -2.58953 | 0.92155 | 0.85523 |
| C | -2.99213 | 2.02138 | -0.02286 |
| C | -3.62031 | 0.48564 | 1.78376 |
| C | -4.28620 | 2.57049 | 0.09971 |
| C | -4.85961 | 1.06496 | 1.85579 |
| H | -3.39983 | -0.32179 | 2.46781 |
| C | -5.22206 | 2.13156 | 1.01102 |
| H | -4.56493 | 3.38859 | -0.55300 |
| H | -5.57268 | 0.69004 | 2.58492 |
| H | -6.20048 | 2.59034 | 1.07353 |
| N | -1.39238 | 0.36482 | 0.80179 |
| O | -0.94280 | 2.26224 | -1.21237 |
| C | -2.12007 | 2.57841 | -1.05120 |
| C | -2.67883 | 3.62775 | -2.01280 |
| H | -2.93085 | 4.55071 | -1.48541 |
| H | -1.90470 | 3.84169 | -2.74719 |
| H | -3.57709 | 3.27618 | -2.52319 |
| I | -1.12945 | -2.59800 | -1.13320 |
| O | 3.47060 | 1.49576 | -0.26396 |
| C | 4.81078 | 1.69359 | -0.08933 |
| C | 5.38436 | 0.70262 | 0.95046 |
| H | 5.19683 | -0.32138 | 0.61123 |
| H | 6.46156 | 0.82950 | 1.11346 |
| H | 4.86535 | 0.84331 | 1.90412 |
| C | 5.09595 | 3.12809 | 0.41141 |
| H | 4.70562 | 3.84619 | -0.31614 |
| H | 4.57383 | 3.28887 | 1.35963 |
| H | 6.16453 | 3.32432 | 0.56125 |
| C | 5.57829 | 1.48974 | -1.41553 |
| H | 6.65931 | 1.64239 | -1.31069 |
| H | 5.40141 | 0.47382 | -1.78241 |
| H | 5.19594 | 2.19142 | -2.16316 |
| K | 1.09748 | 0.97530 | -0.36649 |

**TS: 24-K** + KOtBu in Benzene

46

-1553.7444203

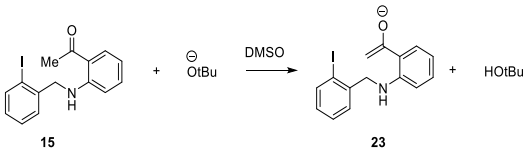
| | | | |
|---|---|---|---|
| C | 1.59155 | 3.19336 | 1.43313 |
| C | 1.02320 | 1.97240 | 1.77692 |
| C | 1.50806 | 0.75842 | 1.27530 |
| C | 2.59334 | 0.82983 | 0.40031 |
| C | 3.18522 | 2.04065 | 0.04714 |
| C | 2.67813 | 3.22844 | 0.56506 |
| H | 1.18253 | 4.11320 | 1.83491 |
| H | 0.16360 | 1.94195 | 2.43894 |
| H | 4.03167 | 2.05779 | -0.62808 |
| H | 3.13412 | 4.17137 | 0.28725 |
| C | 0.75997 | -0.51680 | 1.58866 |
| H | 1.48566 | -1.33151 | 1.76256 |
| H | 0.23560 | -0.36797 | 2.55059 |
| C | -0.98777 | -1.79230 | 0.66593 |
| C | -2.03075 | -2.04992 | -0.30402 |
| C | -0.99550 | -2.66099 | 1.80821 |
| C | -2.98442 | -3.03140 | -0.07717 |
| C | -1.94784 | -3.65576 | 1.98060 |
| H | -0.23088 | -2.54508 | 2.56679 |
| C | -2.96421 | -3.85930 | 1.04980 |
| H | -3.76186 | -3.16928 | -0.82373 |
| H | -1.89637 | -4.28200 | 2.86748 |
| H | -3.71179 | -4.63054 | 1.18911 |
| N | -0.14312 | -0.76961 | 0.49513 |
| O | -1.11473 | -1.17498 | -2.32139 |
| C | -2.11769 | -1.28668 | -1.59386 |
| C | -3.35534 | -0.59925 | -1.89737 |
| H | -3.04733 | 0.60404 | -1.44525 |
| H | -3.51783 | -0.44476 | -2.96486 |
| H | -4.23674 | -0.94753 | -1.36324 |
| I | 3.40348 | -0.93778 | -0.48173 |
| O | -2.60050 | 1.81204 | -1.08236 |
| C | -3.20809 | 2.23694 | 0.09964 |
| C | -2.51063 | 3.51685 | 0.58171 |
| H | -2.58032 | 4.28807 | -0.19120 |
| H | -2.95417 | 3.90368 | 1.50605 |
| H | -1.45163 | 3.30922 | 0.76664 |
| C | -3.08430 | 1.15991 | 1.19365 |
| H | -3.60369 | 0.24597 | 0.89053 |
| H | -2.03063 | 0.89742 | 1.33301 |
| H | -3.50518 | 1.50172 | 2.14585 |
| C | -4.69598 | 2.53761 | -0.14855 |
| H | -5.20448 | 2.87604 | 0.76083 |
| H | -4.79395 | 3.31171 | -0.91534 |
| H | -5.19507 | 1.63403 | -0.51025 |
| K | -0.15334 | 1.09072 | -1.44386 |

**Prod: 25-K** + HOtBu in Benzene

46

-1553.7645147

| | | | |
|---|---|---|---|
| C | -1.51650 | 3.49812 | -0.81323 |
| C | -0.87376 | 2.38029 | -1.33272 |
| C | -1.34918 | 1.08184 | -1.11855 |
| C | -2.50852 | 0.95590 | -0.35115 |
| C | -3.17548 | 2.06067 | 0.17312 |
| C | -2.67289 | 3.33804 | -0.05682 |
| H | -1.11219 | 4.48770 | -0.99233 |
| H | 0.03712 | 2.49620 | -1.91104 |
| H | -4.07734 | 1.92660 | 0.75762 |
| H | -3.18727 | 4.19803 | 0.35566 |
| C | -0.52790 | -0.09517 | -1.59136 |
| H | -1.19931 | -0.85389 | -2.03669 |
| H | 0.11442 | 0.25583 | -2.42184 |
| C | 1.05569 | -1.59865 | -0.70758 |
| C | 1.83203 | -2.14493 | 0.37892 |
| C | 1.25950 | -2.20941 | -1.98206 |
| C | 2.70247 | -3.19589 | 0.16782 |
| C | 2.15628 | -3.26177 | -2.16097 |
| H | 0.70420 | -1.85293 | -2.84186 |
| C | 2.89090 | -3.77385 | -1.09997 |
| H | 3.25901 | -3.57633 | 1.02056 |
| H | 2.27473 | -3.68650 | -3.15458 |
| H | 3.58552 | -4.59364 | -1.23933 |
| N | 0.21470 | -0.57974 | -0.46050 |
| O | 2.35079 | -0.42562 | 1.97667 |
| C | 1.71574 | -1.54325 | 1.75736 |
| C | 0.93745 | -2.16889 | 2.68708 |
| H | 2.53006 | 0.96734 | 1.20203 |
| H | 0.86844 | -1.77283 | 3.69676 |
| H | 0.41928 | -3.08880 | 2.44963 |
| I | -3.32959 | -0.96883 | 0.07564 |
| O | 2.44414 | 1.91864 | 0.90529 |
| C | 3.35036 | 2.13359 | -0.16839 |
| C | 3.06301 | 3.53050 | -0.70687 |
| H | 3.20236 | 4.27432 | 0.08207 |
| H | 3.72927 | 3.77236 | -1.53903 |
| H | 2.02940 | 3.58944 | -1.05728 |
| C | 3.13076 | 1.07639 | -1.25131 |
| H | 3.29129 | 0.07515 | -0.84080 |
| H | 2.09934 | 1.11162 | -1.61011 |
| H | 3.81485 | 1.23188 | -2.09078 |
| C | 4.78426 | 2.05125 | 0.36244 |
| H | 5.51216 | 2.21398 | -0.43754 |
| H | 4.93956 | 2.80385 | 1.13990 |
| H | 4.95944 | 1.06353 | 0.79716 |
| K | 0.06771 | 0.82791 | 1.77454 |




**SM: 15** + tert-butoxide anion in DMSO
46
-954.4014472

| | | | |
|---|---|---|---|
| C | 4.52224 | 2.80138 | 1.45063 |
| C | 3.54106 | 1.94592 | 1.93789 |
| C | 3.12581 | 0.82513 | 1.21543 |
| C | 3.72679 | 0.59444 | -0.02491 |
| C | 4.71225 | 1.43700 | -0.52690 |
| C | 5.10861 | 2.54501 | 0.21702 |
| H | 4.82530 | 3.66349 | 2.03217 |
| H | 3.07972 | 2.14180 | 2.89980 |
| H | 5.17035 | 1.23624 | -1.48715 |
| H | 5.87569 | 3.20216 | -0.17456 |
| C | 2.04303 | -0.06100 | 1.77519 |
| H | 2.34030 | -1.11206 | 1.67816 |
| H | 1.92182 | 0.14892 | 2.84282 |
| C | -0.26778 | -0.66219 | 1.13127 |
| C | -1.38472 | -0.53180 | 0.25119 |
| C | -0.30163 | -1.68664 | 2.10506 |
| C | -2.47146 | -1.40631 | 0.40396 |
| C | -1.39202 | -2.52905 | 2.21664 |
| H | 0.52803 | -1.80122 | 2.78997 |
| C | -2.49479 | -2.39633 | 1.36943 |
| H | -3.32701 | -1.29052 | -0.24944 |
| H | -1.38506 | -3.29779 | 2.98163 |
| H | -3.35084 | -3.05190 | 1.46508 |
| N | 0.80331 | 0.17262 | 1.05786 |
| O | -0.51852 | 1.31102 | -0.95857 |
| C | -1.42410 | 0.49117 | -0.81992 |
| C | -2.61273 | 0.53448 | -1.74166 |
| H | -3.52046 | 0.81033 | -1.17297 |
| H | -2.41872 | 1.27845 | -2.51306 |
| H | -2.78448 | -0.43751 | -2.20963 |
| I | 3.16978 | -1.09114 | -1.21131 |
| O | -5.12217 | 1.47224 | 0.00289 |
| C | -6.32253 | 0.84854 | -0.23280 |
| C | -7.28882 | 1.01814 | 0.96111 |
| H | -7.47031 | 2.08352 | 1.13574 |
| H | -8.25440 | 0.52425 | 0.80132 |
| H | -6.83088 | 0.59936 | 1.86295 |
| C | -6.12618 | -0.66805 | -0.46713 |
| H | -5.44553 | -0.82196 | -1.31137 |
| H | -5.67544 | -1.12112 | 0.42214 |
| H | -7.06608 | -1.18964 | -0.68150 |
| C | -7.01831 | 1.42963 | -1.48619 |
| H | -7.98089 | 0.94989 | -1.69814 |
| H | -7.19008 | 2.50141 | -1.34403 |
| H | -6.36909 | 1.30192 | -2.35858 |
| H | 0.78390 | 0.86132 | 0.31692 |

**TS: 15** + tert-butoxide anion in DMSO
46
-954.3958219

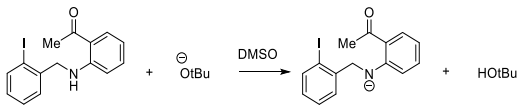
| | | | |
|---|---|---|---|
| C | -5.09263 | -0.62233 | 2.41772 |
| C | -4.17077 | 0.40122 | 2.22939 |
| C | -3.36273 | 0.45692 | 1.09170 |
| C | -3.50811 | -0.56204 | 0.14544 |
| C | -4.42479 | -1.59277 | 0.31573 |
| C | -5.21902 | -1.62054 | 1.45927 |
| H | -5.70751 | -0.63895 | 3.30933 |
| H | -4.06717 | 1.18072 | 2.97643 |
| H | -4.52509 | -2.36713 | -0.43418 |
| H | -5.93451 | -2.42317 | 1.59143 |
| C | -2.36919 | 1.58056 | 0.93436 |
| H | -2.48876 | 2.03539 | -0.05676 |
| H | -2.58742 | 2.35562 | 1.67605 |
| C | 0.05529 | 1.66613 | 0.46641 |
| C | 1.24463 | 0.94336 | 0.16912 |
| C | -0.01008 | 3.02875 | 0.10839 |
| C | 2.31860 | 1.62756 | -0.41203 |
| C | 1.07040 | 3.66832 | -0.47684 |
| H | -0.90735 | 3.59378 | 0.32848 |
| C | 2.25351 | 2.97609 | -0.73177 |
| H | 3.23420 | 1.07968 | -0.60045 |
| H | 0.99088 | 4.72149 | -0.72292 |
| H | 3.10606 | 3.47810 | -1.17194 |
| N | -1.01511 | 1.07354 | 1.08579 |
| O | 0.59977 | -1.06567 | 1.25336 |
| C | 1.36567 | -0.52799 | 0.43501 |
| C | 2.43213 | -1.26618 | -0.22496 |
| H | 3.50604 | -1.01221 | 0.42306 |
| H | 2.25801 | -2.34016 | -0.16251 |
| H | 2.63175 | -0.94566 | -1.24724 |
| I | -2.33910 | -0.56655 | -1.64222 |
| O | 4.65203 | -0.74385 | 1.15411 |
| C | 5.81478 | -0.93029 | 0.41175 |
| C | 7.03927 | -0.70301 | 1.31056 |
| H | 7.01637 | -1.40412 | 2.14984 |
| H | 7.98004 | -0.84180 | 0.76716 |
| H | 7.01785 | 0.31373 | 1.71376 |
| C | 5.87686 | 0.06240 | -0.76509 |
| H | 5.03586 | -0.10812 | -1.44437 |
| H | 5.81149 | 1.08746 | -0.38706 |
| H | 6.80443 | -0.03798 | -1.33823 |
| C | 5.87550 | -2.36271 | -0.15327 |
| H | 6.78736 | -2.53724 | -0.73389 |
| H | 5.84445 | -3.08484 | 0.66832 |
| H | 5.01291 | -2.54541 | -0.80104 |
| H | -0.89188 | 0.08871 | 1.28871 |

**Prod: 23** + HOtBu in DMSO

46

-954.4188824

| | | | |
|---|---|---|---|
| C | -4.82281 | -1.38921 | 2.33045 |
| C | -3.96066 | -0.29889 | 2.37377 |
| C | -3.23401 | 0.10405 | 1.25096 |
| C | -3.40109 | -0.63475 | 0.07666 |
| C | -4.25903 | -1.72647 | 0.01279 |
| C | -4.97091 | -2.10433 | 1.14834 |
| H | -5.37437 | -1.67796 | 3.21697 |
| H | -3.84111 | 0.25973 | 3.29584 |
| H | -4.37548 | -2.27929 | -0.91082 |
| H | -5.63841 | -2.95629 | 1.10008 |
| C | -2.29149 | 1.27864 | 1.34605 |
| H | -2.48350 | 1.96639 | 0.51242 |
| H | -2.50285 | 1.82754 | 2.27055 |
| C | 0.09705 | 1.58555 | 0.77268 |
| C | 1.25944 | 0.97785 | 0.22306 |
| C | -0.00726 | 2.98806 | 0.76567 |
| C | 2.28217 | 1.80750 | -0.23581 |
| C | 1.02152 | 3.78186 | 0.27224 |
| H | -0.89295 | 3.45723 | 1.17797 |
| C | 2.18301 | 3.19772 | -0.22118 |
| H | 3.18391 | 1.34457 | -0.62139 |
| H | 0.91539 | 4.86101 | 0.29085 |
| H | 2.99937 | 3.80938 | -0.58587 |
| N | -0.91737 | 0.81727 | 1.29914 |
| O | 0.82910 | -1.22901 | 1.04832 |
| C | 1.37329 | -0.53045 | 0.11405 |
| C | 2.05475 | -1.05080 | -0.96287 |
| H | 3.72277 | -0.93581 | 0.40147 |
| H | 2.12584 | -2.12777 | -1.07311 |
| H | 2.42125 | -0.42634 | -1.76638 |
| I | -2.35730 | -0.09787 | -1.70722 |
| O | 4.48840 | -0.90300 | 1.00754 |
| C | 5.67783 | -1.10314 | 0.23926 |
| C | 6.83169 | -1.03491 | 1.23072 |
| H | 6.71696 | -1.80792 | 1.99438 |
| H | 7.78603 | -1.18619 | 0.72142 |
| H | 6.84968 | -0.05929 | 1.72248 |
| C | 5.80541 | 0.00105 | -0.81080 |
| H | 4.96557 | -0.04284 | -1.51038 |
| H | 5.80698 | 0.98134 | -0.32722 |
| H | 6.73227 | -0.10930 | -1.37944 |
| C | 5.62684 | -2.47412 | -0.43554 |
| H | 6.54054 | -2.66191 | -1.00512 |
| H | 5.51638 | -3.25873 | 0.31695 |
| H | 4.77528 | -2.52566 | -1.11969 |
| H | -0.72582 | -0.18079 | 1.27692 |




15 24

**SM: 15** + tert-butoxide anion in DMSO

46

-954.405613787

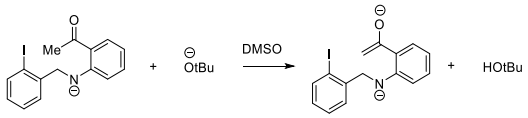
| | | | |
|---|---|---|---|
| C | -2.50846 | 3.42287 | -0.56243 |
| C | -1.59702 | 2.53472 | -1.12373 |
| C | -1.66590 | 1.16035 | -0.88208 |
| C | -2.69999 | 0.70658 | -0.05893 |
| C | -3.62233 | 1.57743 | 0.51013 |
| C | -3.51998 | 2.94330 | 0.26025 |
| H | -2.42706 | 4.48319 | -0.76860 |
| H | -0.81114 | 2.90826 | -1.77066 |
| H | -4.41731 | 1.19966 | 1.14056 |
| H | -4.23742 | 3.62260 | 0.70498 |
| C | -0.62841 | 0.23909 | -1.47724 |
| H | -1.13152 | -0.62133 | -1.92871 |
| H | -0.09305 | 0.76388 | -2.28164 |
| C | 1.21270 | -1.17775 | -0.69643 |
| C | 2.17368 | -1.49731 | 0.30100 |
| C | 1.30065 | -1.83478 | -1.93664 |
| C | 3.19628 | -2.39504 | 0.00334 |
| C | 2.31138 | -2.75698 | -2.18978 |
| H | 0.59081 | -1.60698 | -2.72133 |
| C | 3.27736 | -3.03641 | -1.23083 |
| H | 3.93747 | -2.61993 | 0.76227 |
| H | 2.34959 | -3.24454 | -3.15782 |
| H | 4.07387 | -3.74170 | -1.43183 |
| N | 0.25992 | -0.22369 | -0.43090 |
| O | 0.97279 | -0.90175 | 2.26088 |
| C | 2.05476 | -1.00189 | 1.71237 |
| C | 3.32736 | -0.82740 | 2.50612 |
| H | 4.12647 | -0.41121 | 1.89736 |
| H | 3.11960 | -0.17346 | 3.35087 |
| H | 3.64417 | -1.80135 | 2.89390 |
| I | -2.96149 | -1.37666 | 0.33025 |
| O | 2.09261 | 1.56443 | 0.95833 |
| C | 2.90794 | 2.23538 | 0.07490 |
| C | 4.34585 | 1.67421 | 0.11236 |
| H | 4.32311 | 0.61068 | -0.14738 |
| H | 5.01554 | 2.19037 | -0.58518 |
| H | 4.75584 | 1.77285 | 1.12247 |
| C | 2.97206 | 3.73991 | 0.41724 |
| H | 1.96383 | 4.16579 | 0.37776 |
| H | 3.35536 | 3.86704 | 1.43484 |
| H | 3.61453 | 4.30471 | -0.26831 |
| C | 2.40097 | 2.10255 | -1.37898 |
| H | 3.03398 | 2.64238 | -2.09228 |
| H | 2.37184 | 1.04656 | -1.66692 |
| H | 1.38515 | 2.50314 | -1.44936 |
| H | 0.63904 | 0.51390 | 0.18020 |

**Prod: 24** + HOtBu in DMSO

46

-954.4191446

| | | | |
|---|---|---|---|
| C | 2.66186 | 3.27068 | 0.49524 |
| C | 1.66997 | 2.45757 | 1.03144 |
| C | 1.65086 | 1.07552 | 0.82190 |
| C | 2.68476 | 0.54277 | 0.05015 |
| C | 3.68942 | 1.33394 | -0.49710 |
| C | 3.67365 | 2.70793 | -0.27473 |
| H | 2.64432 | 4.33863 | 0.67751 |
| H | 0.87573 | 2.89603 | 1.62576 |
| H | 4.47987 | 0.88726 | -1.08725 |
| H | 4.45461 | 3.32739 | -0.69940 |
| C | 0.53703 | 0.23859 | 1.40630 |
| H | 0.99488 | -0.62696 | 1.91073 |
| H | 0.04690 | 0.82988 | 2.19810 |
| C | -1.31764 | -1.04252 | 0.71243 |
| C | -2.29364 | -1.54235 | -0.24805 |
| C | -1.48457 | -1.53689 | 2.06230 |
| C | -3.33619 | -2.37825 | 0.18673 |
| C | -2.51249 | -2.37632 | 2.42601 |
| H | -0.79040 | -1.21930 | 2.82870 |
| C | -3.46952 | -2.81013 | 1.49433 |
| H | -4.06192 | -2.72535 | -0.53949 |
| H | -2.58400 | -2.70070 | 3.46030 |
| H | -4.27984 | -3.46624 | 1.78489 |
| N | -0.38639 | -0.16457 | 0.36463 |
| O | -1.22142 | -0.81695 | -2.25199 |
| C | -2.22471 | -1.23322 | -1.68632 |
| C | -3.46983 | -1.46315 | -2.53818 |
| H | -4.37014 | -1.06706 | -2.06602 |
| H | -3.31421 | -0.97527 | -3.49900 |
| H | -3.62469 | -2.53077 | -2.71493 |
| I | 2.81377 | -1.56335 | -0.30150 |
| O | -1.29585 | 2.20501 | -0.78097 |
| C | -2.49617 | 2.62012 | -0.14014 |
| C | -3.67774 | 1.79490 | -0.65514 |
| H | -3.55529 | 0.74622 | -0.37123 |
| H | -4.62104 | 2.15816 | -0.23730 |
| H | -3.73161 | 1.85757 | -1.74556 |
| C | -2.68224 | 4.08983 | -0.50166 |
| H | -1.82947 | 4.67431 | -0.14678 |
| H | -2.75314 | 4.20354 | -1.58659 |
| H | -3.59321 | 4.48998 | -0.05023 |
| C | -2.37388 | 2.45849 | 1.37721 |
| H | -3.28295 | 2.80504 | 1.87637 |
| H | -2.21345 | 1.40759 | 1.63515 |
| H | -1.52932 | 3.04258 | 1.75214 |
| H | -1.02193 | 1.30768 | -0.45128 |




24 25

**SM: 24** + tert-butoxide anion in DMSO

45

-953.8859693

| | | | |
|---|---|---|---|
| C | 4.11576 | 3.27706 | 1.03038 |
| C | 3.11773 | 2.43281 | 1.50374 |
| C | 2.95414 | 1.13248 | 1.01580 |
| C | 3.84355 | 0.71702 | 0.02392 |
| C | 4.85141 | 1.54119 | -0.46579 |
| C | 4.98561 | 2.83036 | 0.04171 |
| H | 4.21447 | 4.27831 | 1.43274 |
| H | 2.43761 | 2.78083 | 2.27456 |
| H | 5.52749 | 1.18560 | -1.23316 |
| H | 5.76992 | 3.47518 | -0.33629 |
| C | 1.82875 | 0.27229 | 1.53963 |
| H | 2.22051 | -0.74467 | 1.70053 |
| H | 1.55038 | 0.65316 | 2.53579 |
| C | -0.29735 | -0.49134 | 0.88249 |
| C | -1.47883 | -0.57924 | 0.01908 |
| C | -0.34090 | -1.34889 | 2.05783 |
| C | -2.51715 | -1.47029 | 0.35895 |
| C | -1.38702 | -2.19275 | 2.33237 |
| H | 0.48457 | -1.31965 | 2.75627 |
| C | -2.50405 | -2.27699 | 1.47888 |
| H | -3.38359 | -1.52542 | -0.28803 |
| H | -1.34935 | -2.80358 | 3.23030 |
| H | -3.32921 | -2.94329 | 1.69633 |
| N | 0.71922 | 0.30394 | 0.60867 |
| O | -0.83158 | 1.04712 | -1.60411 |
| C | -1.64781 | 0.22196 | -1.19742 |
| C | -2.92280 | 0.04388 | -2.02111 |
| H | -3.80972 | 0.30614 | -1.43603 |
| H | -2.85404 | 0.70476 | -2.88393 |
| H | -3.03982 | -0.98462 | -2.37046 |
| I | 3.71707 | -1.25439 | -0.80014 |
| O | -5.48699 | 1.27436 | 0.44631 |
| C | -6.61095 | 0.74010 | -0.13240 |
| C | -7.87402 | 1.03605 | 0.71090 |
| H | -7.99421 | 2.11855 | 0.82259 |
| H | -8.78901 | 0.63097 | 0.26306 |
| H | -7.75854 | 0.60235 | 1.70955 |
| C | -6.49599 | -0.79625 | -0.27592 |
| H | -5.64242 | -1.04268 | -0.91546 |
| H | -6.32324 | -1.24317 | 0.70883 |
| H | -7.39401 | -1.25083 | -0.71042 |
| C | -6.84591 | 1.32308 | -1.54616 |
| H | -7.73533 | 0.90777 | -2.03417 |
| H | -6.96364 | 2.40970 | -1.47976 |
| H | -5.97485 | 1.11285 | -2.17501 |

**TS: 24** + tert-butoxide anion in DMSO

45

-953.8762757

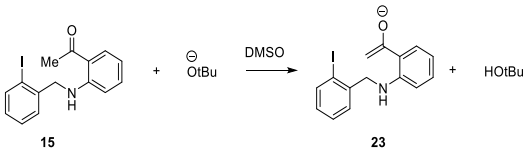
| | | | |
|---|---|---|---|
| C | -1.93307 | 3.62466 | -0.85019 |
| C | -1.24174 | 2.50552 | -1.30053 |
| C | -1.63397 | 1.20582 | -0.96316 |
| C | -2.75613 | 1.08205 | -0.14378 |
| C | -3.46680 | 2.18480 | 0.31890 |
| C | -3.04992 | 3.46417 | -0.03762 |
| H | -1.60102 | 4.61680 | -1.13230 |
| H | -0.36720 | 2.62742 | -1.93203 |
| H | -4.33515 | 2.05320 | 0.95222 |
| H | -3.60124 | 4.32550 | 0.32049 |
| C | -0.81163 | 0.03173 | -1.43692 |
| H | -1.50141 | -0.75504 | -1.79353 |
| H | -0.24706 | 0.35654 | -2.33021 |
| C | 0.82258 | -1.46132 | -0.66089 |
| C | 1.76804 | -1.96280 | 0.31714 |
| C | 0.84661 | -2.14980 | -1.92466 |
| C | 2.64325 | -2.98971 | 0.00720 |
| C | 1.72100 | -3.19801 | -2.18668 |
| H | 0.16745 | -1.84207 | -2.71006 |
| C | 2.63759 | -3.64001 | -1.23549 |
| H | 3.35129 | -3.30866 | 0.76857 |
| H | 1.68525 | -3.67533 | -3.16258 |
| H | 3.32165 | -4.45344 | -1.44331 |
| N | 0.04797 | -0.41649 | -0.36972 |
| O | 0.85315 | -1.43946 | 2.45464 |
| C | 1.83696 | -1.37912 | 1.70473 |
| C | 3.07707 | -0.71813 | 2.07533 |
| H | 3.02058 | 0.48835 | 1.57914 |
| H | 3.19950 | -0.61566 | 3.15592 |
| H | 3.96006 | -1.13572 | 1.59125 |
| I | -3.46627 | -0.84633 | 0.45506 |
| O | 3.01671 | 1.76772 | 1.12220 |
| C | 3.99301 | 1.95673 | 0.14519 |
| C | 3.87738 | 3.37623 | -0.42946 |
| H | 4.01076 | 4.11464 | 0.36667 |
| H | 4.62719 | 3.56344 | -1.20583 |
| H | 2.88388 | 3.51750 | -0.86557 |
| C | 3.82059 | 0.94706 | -1.00737 |
| H | 3.87045 | -0.07637 | -0.62403 |
| H | 2.83761 | 1.08012 | -1.47124 |
| H | 4.58909 | 1.07462 | -1.77730 |
| C | 5.40031 | 1.78256 | 0.74859 |
| H | 6.18880 | 1.93553 | 0.00422 |
| H | 5.54429 | 2.50288 | 1.55958 |
| H | 5.50620 | 0.77614 | 1.16315 |

**Prod: 25** + HOtBu in DMSO

45

-953.8958041

| | | | |
|---|---|---|---|
| C | -1.63245 | 3.64037 | -0.44529 |
| C | -0.95311 | 2.52965 | -0.93191 |
| C | -1.44371 | 1.22899 | -0.77160 |
| C | -2.65498 | 1.09692 | -0.09317 |
| C | -3.35778 | 2.19148 | 0.40113 |
| C | -2.84040 | 3.47118 | 0.22356 |
| H | -1.22162 | 4.63306 | -0.58810 |
| H | -0.00899 | 2.65773 | -1.45243 |
| H | -4.29904 | 2.05221 | 0.91800 |
| H | -3.38499 | 4.32621 | 0.60610 |
| C | -0.62922 | 0.06243 | -1.27419 |
| H | -1.31899 | -0.67183 | -1.72935 |
| H | -0.00020 | 0.42832 | -2.10865 |
| C | 0.92690 | -1.52172 | -0.52620 |
| C | 1.83585 | -2.09439 | 0.44908 |
| C | 0.97260 | -2.12721 | -1.82847 |
| C | 2.67344 | -3.13868 | 0.10139 |
| C | 1.82374 | -3.18806 | -2.13267 |
| H | 0.32926 | -1.75041 | -2.61405 |
| C | 2.68908 | -3.71561 | -1.18209 |
| H | 3.34794 | -3.52286 | 0.86295 |
| H | 1.80521 | -3.60213 | -3.13768 |
| H | 3.35345 | -4.53905 | -1.41592 |
| N | 0.15218 | -0.48307 | -0.19396 |
| O | 0.89071 | -1.77523 | 2.63067 |
| C | 1.89677 | -1.56668 | 1.86823 |
| C | 3.06349 | -0.92011 | 2.23873 |
| H | 2.93693 | 1.06649 | 1.43705 |
| H | 3.20553 | -0.58831 | 3.26427 |
| H | 3.91413 | -0.89599 | 1.56800 |
| I | -3.52743 | -0.83272 | 0.22228 |
| O | 2.94076 | 1.99510 | 1.12835 |
| C | 3.76656 | 2.08958 | -0.03594 |
| C | 3.59019 | 3.51030 | -0.55689 |
| H | 3.89751 | 4.23295 | 0.20319 |
| H | 4.19465 | 3.66944 | -1.45291 |
| H | 2.54187 | 3.69211 | -0.80599 |
| C | 3.31295 | 1.07219 | -1.08362 |
| H | 3.37434 | 0.05437 | -0.68559 |
| H | 2.26943 | 1.25028 | -1.35814 |
| H | 3.93504 | 1.14048 | -1.98022 |
| C | 5.22602 | 1.84299 | 0.35076 |
| H | 5.88088 | 1.94027 | -0.51907 |
| H | 5.54185 | 2.56507 | 1.10787 |
| H | 5.34671 | 0.83660 | 0.76025 |




15 23

**SM: 15** + tert-butoxide anion in Benzene
46
-954.3624541

| | | | |
|---|---|---|---|
| C | -5.11516 | -0.37059 | 2.42726 |
| C | -4.09437 | 0.56235 | 2.28366 |
| C | -3.28074 | 0.58724 | 1.14946 |
| C | -3.52497 | -0.36618 | 0.15617 |
| C | -4.54078 | -1.30611 | 0.28338 |
| C | -5.33654 | -1.30735 | 1.42561 |
| H | -5.72945 | -0.36794 | 3.31966 |
| H | -3.91314 | 1.29178 | 3.06581 |
| H | -4.71206 | -2.03386 | -0.49976 |
| H | -6.12511 | -2.04369 | 1.52555 |
| C | -2.17071 | 1.60458 | 1.04067 |
| H | -2.24828 | 2.11596 | 0.07363 |
| H | -2.30299 | 2.36172 | 1.82162 |
| C | 0.22091 | 1.39375 | 0.45271 |
| C | 1.28491 | 0.51612 | 0.09517 |
| C | 0.31247 | 2.74559 | 0.07426 |
| C | 2.40499 | 1.02791 | -0.57559 |
| C | 1.42765 | 3.22054 | -0.59915 |
| H | -0.48153 | 3.43035 | 0.34562 |
| C | 2.48488 | 2.37153 | -0.91670 |
| H | 3.25946 | 0.37967 | -0.79473 |
| H | 1.47397 | 4.27206 | -0.86337 |
| H | 3.36720 | 2.74752 | -1.42010 |
| N | -0.88066 | 0.94940 | 1.14289 |
| O | 0.39611 | -1.40090 | 1.17250 |
| C | 1.21212 | -0.94182 | 0.37713 |
| C | 2.12616 | -1.86253 | -0.38047 |
| H | 3.18304 | -1.54757 | -0.35190 |
| H | 1.99964 | -2.87252 | 0.00740 |
| H | 1.83771 | -1.84105 | -1.43731 |
| I | -2.35872 | -0.40239 | -1.62841 |
| O | 4.99999 | -0.66947 | -0.78205 |
| C | 5.75437 | -0.66325 | 0.35493 |
| C | 7.11358 | 0.03939 | 0.12398 |
| H | 6.93336 | 1.06844 | -0.20266 |
| H | 7.74521 | 0.06028 | 1.02132 |
| H | 7.65386 | -0.47904 | -0.67438 |
| C | 6.04415 | -2.10668 | 0.83763 |
| H | 5.09599 | -2.61966 | 1.02907 |
| H | 6.56814 | -2.64938 | 0.04463 |
| H | 6.65150 | -2.14218 | 1.75096 |
| C | 5.02948 | 0.08002 | 1.50685 |
| H | 5.60723 | 0.08898 | 2.43947 |
| H | 4.83218 | 1.11427 | 1.20642 |
| H | 4.06376 | -0.40014 | 1.70115 |
| H | -0.86615 | -0.03720 | 1.37203 |

**TS: 15** + tert-butoxide anion in Benzene
46
-954.3559457

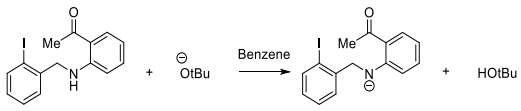
| | | | |
|---|---|---|---|
| C | -5.37903 | -0.33224 | 1.92442 |
| C | -4.50559 | 0.71612 | 1.65847 |
| C | -3.49329 | 0.60119 | 0.70410 |
| C | -3.38125 | -0.61447 | 0.02271 |
| C | -4.24689 | -1.67228 | 0.27444 |
| C | -5.24813 | -1.52874 | 1.23088 |
| H | -6.15272 | -0.21506 | 2.67372 |
| H | -4.59757 | 1.64997 | 2.20262 |
| H | -4.14143 | -2.60383 | -0.26698 |
| H | -5.91867 | -2.35638 | 1.42943 |
| C | -2.54873 | 1.75442 | 0.46815 |
| H | -2.49008 | 1.95886 | -0.60822 |
| H | -2.95857 | 2.65072 | 0.94769 |
| C | -0.08396 | 1.87160 | 0.34948 |
| C | 1.11339 | 1.11033 | 0.37950 |
| C | -0.08779 | 3.09333 | -0.34626 |
| C | 2.26636 | 1.63476 | -0.20932 |
| C | 1.06816 | 3.57741 | -0.94280 |
| H | -0.99768 | 3.68115 | -0.38318 |
| C | 2.26000 | 2.86237 | -0.86144 |
| H | 3.18866 | 1.06774 | -0.12430 |
| H | 1.03746 | 4.53136 | -1.45847 |
| H | 3.17063 | 3.25207 | -1.30022 |
| N | -1.22954 | 1.42991 | 0.97623 |
| O | 0.36491 | -0.55693 | 1.89208 |
| C | 1.15434 | -0.26695 | 0.98317 |
| C | 2.16464 | -1.18598 | 0.47669 |
| H | 3.31670 | -0.81217 | 0.86869 |
| H | 1.97844 | -2.20079 | 0.82748 |
| H | 2.26091 | -1.14071 | -0.61049 |
| I | -1.87617 | -0.89605 | -1.45968 |
| O | 4.59653 | -0.37603 | 1.21117 |
| C | 5.58033 | -0.88382 | 0.38292 |
| C | 6.96425 | -0.56608 | 0.97451 |
| H | 7.04997 | -1.02006 | 1.96586 |
| H | 7.78088 | -0.93762 | 0.34419 |
| H | 7.07121 | 0.51664 | 1.08693 |
| C | 5.49495 | -0.25243 | -1.02383 |
| H | 4.51845 | -0.46688 | -1.46954 |
| H | 5.59930 | 0.83426 | -0.94119 |
| H | 6.27264 | -0.62825 | -1.69840 |
| C | 5.45022 | -2.41558 | 0.23883 |
| H | 6.24006 | -2.83989 | -0.39143 |
| H | 5.50410 | -2.87820 | 1.22873 |
| H | 4.48171 | -2.66957 | -0.20172 |
| H | -1.11437 | 0.55389 | 1.47418 |

**Prod: 23** + HOtBu in Benzene

46

-954.3766453

| | | | |
|---|---|---|---|
| C | -5.01236 | -1.27271 | 2.15978 |
| C | -4.18708 | -0.15400 | 2.19364 |
| C | -3.35978 | 0.17880 | 1.11969 |
| C | -3.38523 | -0.65988 | 0.00144 |
| C | -4.20413 | -1.78143 | -0.05068 |
| C | -5.01872 | -2.08883 | 1.03559 |
| H | -5.64010 | -1.50893 | 3.01071 |
| H | -4.17131 | 0.48082 | 3.07325 |
| H | -4.20587 | -2.41417 | -0.92939 |
| H | -5.65185 | -2.96745 | 0.99685 |
| C | -2.45649 | 1.38659 | 1.20821 |
| H | -2.59512 | 2.00175 | 0.30982 |
| H | -2.76861 | 1.99653 | 2.06626 |
| C | -0.04195 | 1.67383 | 0.73455 |
| C | 1.16132 | 1.00425 | 0.37782 |
| C | -0.15544 | 3.05330 | 0.49017 |
| C | 2.21045 | 1.76650 | -0.12893 |
| C | 0.90227 | 3.77415 | -0.05346 |
| H | -1.06978 | 3.56912 | 0.76030 |
| C | 2.10087 | 3.13884 | -0.35361 |
| H | 3.14439 | 1.26383 | -0.35457 |
| H | 0.78887 | 4.84009 | -0.22082 |
| H | 2.94054 | 3.69718 | -0.75042 |
| N | -1.07815 | 0.97175 | 1.30499 |
| O | 0.63602 | -1.05023 | 1.48370 |
| C | 1.27880 | -0.50436 | 0.52187 |
| C | 2.06328 | -1.17549 | -0.39529 |
| H | 3.85222 | -0.85777 | 0.73023 |
| H | 2.10544 | -2.25807 | -0.34658 |
| H | 2.45419 | -0.68257 | -1.27574 |
| I | -2.17679 | -0.23229 | -1.70024 |
| O | 4.72679 | -0.73644 | 1.15618 |
| C | 5.74652 | -1.04378 | 0.21461 |
| C | 7.06132 | -0.94089 | 0.97958 |
| H | 7.06511 | -1.64925 | 1.81123 |
| H | 7.90904 | -1.16030 | 0.32535 |
| H | 7.17983 | 0.06698 | 1.38440 |
| C | 5.72197 | -0.03177 | -0.93358 |
| H | 4.77521 | -0.09855 | -1.47572 |
| H | 5.82406 | 0.98158 | -0.53688 |
| H | 6.53701 | -0.21778 | -1.63885 |
| C | 5.55356 | -2.46240 | -0.32530 |
| H | 6.35590 | -2.72789 | -1.01964 |
| H | 5.55141 | -3.17737 | 0.50098 |
| H | 4.59760 | -2.53882 | -0.84925 |
| H | -0.83879 | -0.00093 | 1.51053 |




15 24

**SM: 15** + tert-butoxide anion in Benzene

46

-954.3636946

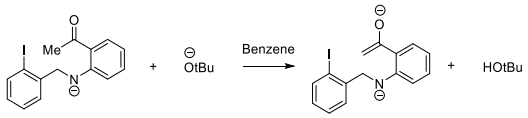
| | | | |
|---|---|---|---|
| C | -1.88415 | 3.56066 | 0.70822 |
| C | -1.02074 | 2.71512 | 0.02208 |
| C | -1.39266 | 1.40052 | -0.28477 |
| C | -2.64155 | 0.96532 | 0.15352 |
| C | -3.52140 | 1.79867 | 0.83542 |
| C | -3.13834 | 3.10842 | 1.10571 |
| H | -1.57250 | 4.57203 | 0.94259 |
| H | -0.00651 | 3.01307 | -0.24768 |
| H | -4.48681 | 1.43191 | 1.16002 |
| H | -3.81855 | 3.76220 | 1.63964 |
| C | -0.40264 | 0.52459 | -1.02077 |
| H | -0.94260 | -0.20303 | -1.62004 |
| H | 0.20106 | 1.15764 | -1.67772 |
| C | 1.02396 | -1.35419 | -0.23921 |
| C | 2.05756 | -1.82805 | 0.63011 |
| C | 0.61893 | -2.22123 | -1.28502 |
| C | 2.64992 | -3.07231 | 0.38435 |
| C | 1.20921 | -3.45629 | -1.47477 |
| H | -0.16285 | -1.91645 | -1.96572 |
| C | 2.24299 | -3.89991 | -0.64889 |
| H | 3.44249 | -3.41091 | 1.04090 |
| H | 0.86399 | -4.08019 | -2.29249 |
| H | 2.71213 | -4.86264 | -0.80652 |
| N | 0.47000 | -0.12651 | -0.05626 |
| O | 1.76944 | -0.25529 | 2.38777 |
| C | 2.47834 | -1.07964 | 1.84757 |
| C | 3.83600 | -1.39836 | 2.45321 |
| H | 4.60762 | -1.49374 | 1.68810 |
| H | 4.09004 | -0.59312 | 3.13986 |
| H | 3.78826 | -2.33579 | 3.01408 |
| I | -3.26442 | -1.06141 | -0.15029 |
| O | 1.93448 | 2.27260 | -0.12724 |
| C | 3.13544 | 2.18121 | -0.77334 |
| C | 4.13118 | 1.28701 | 0.00397 |
| H | 3.74983 | 0.26101 | 0.02540 |
| H | 5.13125 | 1.26890 | -0.44699 |
| H | 4.21081 | 1.64589 | 1.03479 |
| C | 3.77848 | 3.57709 | -0.94099 |
| H | 3.09271 | 4.22263 | -1.49874 |
| H | 3.93339 | 4.02130 | 0.04717 |
| H | 4.73992 | 3.54570 | -1.46868 |
| C | 2.96212 | 1.55850 | -2.18123 |
| H | 3.91017 | 1.45351 | -2.72339 |
| H | 2.50880 | 0.56561 | -2.07966 |
| H | 2.28819 | 2.18396 | -2.77626 |
| H | 1.07615 | 0.58962 | 0.37553 |

**Prod: 24** + HOtBu in Benzene

46

-954.3791836

| | | | |
|---|---|---|---|
| C | 2.50784 | 3.18917 | 0.85635 |
| C | 1.57952 | 2.27682 | 1.34616 |
| C | 1.61672 | 0.92287 | 1.00204 |
| C | 2.64207 | 0.51828 | 0.14607 |
| C | 3.58525 | 1.41058 | -0.35216 |
| C | 3.51312 | 2.75468 | 0.00129 |
| H | 2.44231 | 4.23362 | 1.13868 |
| H | 0.79176 | 2.61406 | 2.01251 |
| H | 4.36892 | 1.06284 | -1.01333 |
| H | 4.24391 | 3.45176 | -0.39212 |
| C | 0.54765 | -0.01138 | 1.51626 |
| H | 1.03283 | -0.92096 | 1.90953 |
| H | 0.06786 | 0.47129 | 2.38767 |
| C | -1.38905 | -1.12014 | 0.77482 |
| C | -2.39942 | -1.44694 | -0.21255 |
| C | -1.61872 | -1.66518 | 2.08513 |
| C | -3.55684 | -2.12643 | 0.15945 |
| C | -2.76652 | -2.37012 | 2.39955 |
| H | -0.87954 | -1.50917 | 2.86062 |
| C | -3.76918 | -2.59861 | 1.45324 |
| H | -4.30202 | -2.33953 | -0.60130 |
| H | -2.88804 | -2.74774 | 3.41118 |
| H | -4.66879 | -3.14511 | 1.70663 |
| N | -0.38551 | -0.30642 | 0.45772 |
| O | -1.13009 | -1.37644 | -2.22285 |
| C | -2.19239 | -1.18563 | -1.66333 |
| C | -3.36509 | -0.68710 | -2.49403 |
| H | -4.32115 | -0.70872 | -1.97446 |
| H | -3.12588 | 0.35260 | -2.73192 |
| H | -3.42284 | -1.25314 | -3.42545 |
| I | 2.84183 | -1.52681 | -0.42316 |
| O | -1.58034 | 1.61592 | -1.06092 |
| C | -2.31062 | 2.53786 | -0.27103 |
| C | -3.66615 | 2.72646 | -0.95298 |
| H | -4.21820 | 1.78318 | -0.94388 |
| H | -4.26188 | 3.49059 | -0.44540 |
| H | -3.51773 | 3.02976 | -1.99303 |
| C | -1.55497 | 3.87012 | -0.23540 |
| H | -0.56870 | 3.72521 | 0.21255 |
| H | -1.41427 | 4.24220 | -1.25353 |
| H | -2.09901 | 4.62373 | 0.34242 |
| C | -2.52273 | 2.01600 | 1.15200 |
| H | -3.13828 | 2.71698 | 1.72317 |
| H | -3.01946 | 1.04215 | 1.13115 |
| H | -1.56654 | 1.89289 | 1.66692 |
| H | -1.05336 | 0.97385 | -0.49999 |




24 25

**SM: 24** + tert-butoxide anion in Benzene

45

-953.7725938

| | | | |
|---|---|---|---|
| C | -5.10006 | -2.03338 | -1.42362 |
| C | -4.01896 | -2.20136 | -0.56712 |
| C | -3.35481 | -1.11680 | 0.01487 |
| C | -3.82831 | 0.15283 | -0.31237 |
| C | -4.91012 | 0.34992 | -1.16485 |
| C | -5.54932 | -0.75189 | -1.72402 |
| H | -5.58463 | -2.89864 | -1.86129 |
| H | -3.65398 | -3.19814 | -0.34215 |
| H | -5.24877 | 1.35226 | -1.39558 |
| H | -6.38836 | -0.60187 | -2.39361 |
| C | -2.14837 | -1.36450 | 0.88954 |
| H | -2.19727 | -0.67738 | 1.75512 |
| H | -2.25086 | -2.38158 | 1.31312 |
| C | 0.18691 | -1.30928 | 0.75898 |
| C | 1.46714 | -1.11501 | 0.08852 |
| C | 0.28719 | -1.57773 | 2.17572 |
| C | 2.66098 | -1.10278 | 0.81331 |
| C | 1.49664 | -1.59049 | 2.84639 |
| H | -0.61448 | -1.78062 | 2.73995 |
| C | 2.70260 | -1.34078 | 2.18694 |
| H | 3.60531 | -0.93922 | 0.29414 |
| H | 1.49933 | -1.80053 | 3.91396 |
| H | 3.64884 | -1.34888 | 2.71429 |
| N | -0.95889 | -1.20229 | 0.09835 |
| O | 0.82868 | -1.50844 | -2.17878 |
| C | 1.57034 | -0.95168 | -1.38411 |
| C | 2.66990 | -0.04233 | -1.90621 |
| H | 3.67505 | -0.37964 | -1.61693 |
| H | 2.59261 | 0.00805 | -2.99293 |
| H | 2.54487 | 0.95868 | -1.48126 |
| I | -2.90087 | 1.90034 | 0.49750 |
| O | 5.73447 | -0.64638 | -0.70927 |
| C | 6.22914 | 0.59445 | -0.46331 |
| C | 7.69676 | 0.53071 | 0.03791 |
| H | 8.31006 | 0.03057 | -0.71905 |
| H | 8.12784 | 1.51946 | 0.24589 |
| H | 7.73263 | -0.06926 | 0.95297 |
| C | 5.39737 | 1.33206 | 0.61862 |
| H | 4.35972 | 1.41662 | 0.28112 |
| H | 5.39752 | 0.73831 | 1.53865 |
| H | 5.77874 | 2.33673 | 0.84551 |
| C | 6.21380 | 1.47532 | -1.74207 |
| H | 6.61530 | 2.48427 | -1.57748 |
| H | 6.80636 | 0.98298 | -2.52024 |
| H | 5.18473 | 1.56108 | -2.10464 |

**TS: 24** + tert-butoxide anion in Benzene

45

-953.7658645

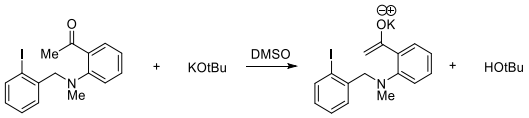
| | | | |
|---|---|---|---|
| C | 1.09079 | -2.93380 | 1.21116 |
| C | 0.58676 | -1.66583 | 0.95068 |
| C | 1.40870 | -0.62680 | 0.49783 |
| C | 2.75540 | -0.93525 | 0.32096 |
| C | 3.28859 | -2.19391 | 0.57587 |
| C | 2.44389 | -3.20348 | 1.02709 |
| H | 0.42182 | -3.71405 | 1.55734 |
| H | -0.46217 | -1.42328 | 1.07828 |
| H | 4.34316 | -2.38503 | 0.42282 |
| H | 2.84776 | -4.18962 | 1.22721 |
| C | 0.81436 | 0.74153 | 0.21969 |
| H | 1.42070 | 1.47761 | 0.78724 |
| H | 1.03149 | 0.97233 | -0.84485 |
| C | -1.20644 | 1.91251 | 0.25286 |
| C | -2.64239 | 2.02058 | 0.45968 |
| C | -0.58383 | 3.08893 | -0.30440 |
| C | -3.31761 | 3.17465 | 0.09795 |
| C | -1.30128 | 4.23147 | -0.62900 |
| H | 0.48673 | 3.08894 | -0.47233 |
| C | -2.67974 | 4.30263 | -0.44037 |
| H | -4.39098 | 3.20825 | 0.26369 |
| H | -0.76822 | 5.08521 | -1.04201 |
| H | -3.24218 | 5.19282 | -0.69658 |
| N | -0.57417 | 0.78224 | 0.53420 |
| O | -3.07131 | 0.49258 | 2.23446 |
| C | -3.44396 | 0.93420 | 1.14322 |
| C | -4.65119 | 0.45282 | 0.47676 |
| H | -4.43002 | -0.60060 | -0.27499 |
| H | -5.38357 | 0.08009 | 1.19758 |
| H | -5.08779 | 1.16382 | -0.22491 |
| I | 4.12299 | 0.56341 | -0.39008 |
| O | -4.46470 | -1.69330 | -1.06689 |
| C | -3.30805 | -2.44883 | -0.95859 |
| C | -3.01243 | -2.78978 | 0.51718 |
| H | -3.84829 | -3.36364 | 0.93188 |
| H | -2.09402 | -3.38068 | 0.62308 |
| H | -2.90812 | -1.86988 | 1.10024 |
| C | -2.10168 | -1.68782 | -1.54155 |
| H | -2.31549 | -1.42483 | -2.58292 |
| H | -1.92020 | -0.76923 | -0.97429 |
| H | -1.18202 | -2.28629 | -1.51116 |
| C | -3.48883 | -3.76351 | -1.73796 |
| H | -2.59651 | -4.39956 | -1.68639 |
| H | -4.34078 | -4.31717 | -1.33073 |
| H | -3.69856 | -3.53761 | -2.78816 |

**Prod: 25** + HOtBu in Benzene

45

-953.7711490

| | | | |
|---|---|---|---|
| C | -1.58567 | 3.61594 | -0.40165 |
| C | -0.91583 | 2.50388 | -0.89588 |
| C | -1.42496 | 1.20754 | -0.76394 |
| C | -2.64286 | 1.08209 | -0.09876 |
| C | -3.33875 | 2.17835 | 0.40148 |
| C | -2.80523 | 3.45399 | 0.24793 |
| H | -1.15305 | 4.60369 | -0.51479 |
| H | 0.04385 | 2.62223 | -1.38857 |
| H | -4.28360 | 2.03902 | 0.91195 |
| H | -3.34053 | 4.31030 | 0.64204 |
| C | -0.61406 | 0.03829 | -1.26873 |
| H | -1.30872 | -0.69705 | -1.71969 |
| H | 0.00845 | 0.40363 | -2.11348 |
| C | 0.93734 | -1.52937 | -0.50522 |
| C | 1.85857 | -2.07374 | 0.47656 |
| C | 0.98318 | -2.15520 | -1.79905 |
| C | 2.69576 | -3.11948 | 0.14282 |
| C | 1.83675 | -3.21900 | -2.08757 |
| H | 0.33389 | -1.79510 | -2.58838 |
| C | 2.70642 | -3.72504 | -1.13073 |
| H | 3.37774 | -3.48068 | 0.90919 |
| H | 1.81627 | -3.65148 | -3.08602 |
| H | 3.37359 | -4.55103 | -1.35129 |
| N | 0.16659 | -0.48740 | -0.18836 |
| O | 0.96449 | -1.71307 | 2.66912 |
| C | 1.93902 | -1.50913 | 1.88822 |
| C | 3.11523 | -0.83128 | 2.20421 |
| H | 2.86431 | 1.13136 | 1.45257 |
| H | 3.28137 | -0.48715 | 3.22223 |
| H | 3.95641 | -0.84781 | 1.52070 |
| I | -3.51805 | -0.84444 | 0.20738 |
| O | 2.95132 | 2.06527 | 1.15202 |
| C | 3.67424 | 2.09626 | -0.06994 |
| C | 3.48810 | 3.50597 | -0.62490 |
| H | 3.85496 | 4.24391 | 0.09400 |
| H | 4.03147 | 3.62907 | -1.56596 |
| H | 2.42665 | 3.69557 | -0.80224 |
| C | 3.12567 | 1.06050 | -1.05225 |
| H | 3.24627 | 0.04794 | -0.65773 |
| H | 2.05384 | 1.21135 | -1.20130 |
| H | 3.64318 | 1.13136 | -2.01438 |
| C | 5.16007 | 1.83413 | 0.20170 |
| H | 5.74395 | 1.88407 | -0.72271 |
| H | 5.54729 | 2.57610 | 0.90571 |
| H | 5.28836 | 0.84200 | 0.64072 |




18 22-K

**SM: 18** + KOtBu in DMSO
50
-1593.5746123

| | | | |
|---|---|---|---|
| C | -2.62969 | 3.45668 | -0.10318 |
| C | -1.85846 | 2.36100 | -0.45808 |
| C | -2.37847 | 1.06219 | -0.48742 |
| C | -3.72443 | 0.90971 | -0.15381 |
| C | -4.51848 | 1.99882 | 0.20272 |
| C | -3.96800 | 3.27336 | 0.23109 |
| H | -2.19230 | 4.44736 | -0.09232 |
| H | -0.81994 | 2.50482 | -0.73050 |
| H | -5.55967 | 1.85231 | 0.45891 |
| H | -4.58739 | 4.11702 | 0.51073 |
| C | -1.44392 | -0.06443 | -0.87231 |
| H | -2.00871 | -0.97800 | -1.08607 |
| H | -0.92962 | 0.23030 | -1.78987 |
| C | 0.63819 | -1.12612 | -0.15509 |
| C | 1.71045 | -1.34037 | 0.75756 |
| C | 0.69420 | -1.80167 | -1.39023 |
| C | 2.69446 | -2.29075 | 0.45745 |
| C | 1.72110 | -2.68805 | -1.68292 |
| H | -0.09042 | -1.67037 | -2.12147 |
| C | 2.71849 | -2.96385 | -0.75279 |
| H | 3.48578 | -2.46953 | 1.17563 |
| H | 1.71776 | -3.19274 | -2.64228 |
| H | 3.50428 | -3.67532 | -0.97107 |
| N | -0.43314 | -0.29909 | 0.16457 |
| O | 1.64017 | 0.70589 | 1.94285 |
| C | 1.96322 | -0.47060 | 1.94381 |
| C | 2.70419 | -1.04748 | 3.12588 |
| H | 3.78066 | -0.98740 | 2.93917 |
| H | 2.47911 | -0.44242 | 4.00237 |
| H | 2.44447 | -2.09067 | 3.30409 |
| I | -4.69208 | -0.99755 | -0.15498 |
| O | 4.45689 | 1.15103 | -0.56506 |
| C | 5.74338 | 0.66582 | -0.50247 |
| C | 6.77052 | 1.80019 | -0.70117 |
| H | 6.63310 | 2.55983 | 0.07478 |
| H | 7.80517 | 1.44268 | -0.65599 |
| H | 6.61066 | 2.27432 | -1.67459 |
| C | 5.98254 | -0.39762 | -1.59459 |
| H | 5.27208 | -1.22012 | -1.46308 |
| H | 5.81337 | 0.04589 | -2.58091 |
| H | 6.99854 | -0.80680 | -1.56787 |
| C | 6.01119 | 0.01087 | 0.86842 |
| H | 7.03131 | -0.37751 | 0.96207 |
| H | 5.84205 | 0.74308 | 1.66455 |
| H | 5.31184 | -0.81866 | 1.01152 |
| K | 2.13468 | 1.76926 | -0.52172 |
| C | -0.96839 | -0.33482 | 1.52989 |
| H | -0.44023 | -1.08075 | 2.12261 |
| H | -0.87635 | 0.63366 | 2.02420 |
| H | -2.02103 | -0.62571 | 1.50141 |

**TS: 18** + KOtBu in DMSO
50
-1593.5721910

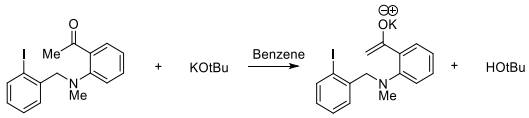
| | | | |
|---|---|---|---|
| C | 0.95590 | -3.15627 | -0.23896 |
| C | 0.51235 | -1.87228 | -0.52073 |
| C | 1.37618 | -0.76885 | -0.50436 |
| C | 2.71657 | -1.01292 | -0.20508 |
| C | 3.18157 | -2.29717 | 0.07643 |
| C | 2.29921 | -3.36932 | 0.06096 |
| H | 0.25822 | -3.98595 | -0.25749 |
| H | -0.54105 | -1.69865 | -0.73179 |
| H | 4.22639 | -2.45975 | 0.30722 |
| H | 2.66561 | -4.36496 | 0.28026 |
| C | 0.77643 | 0.58088 | -0.83078 |
| H | 1.56926 | 1.29444 | -1.08164 |
| H | 0.14402 | 0.46448 | -1.71321 |
| C | -1.00769 | 2.08124 | -0.15738 |
| C | -2.28553 | 2.16734 | 0.42585 |
| C | -0.67907 | 2.97663 | -1.17961 |
| C | -3.18688 | 3.13104 | -0.03052 |
| C | -1.58224 | 3.94041 | -1.61591 |
| H | 0.29640 | 2.92446 | -1.64709 |
| C | -2.84223 | 4.02524 | -1.03704 |
| H | -4.17416 | 3.17724 | 0.41624 |
| H | -1.29631 | 4.62046 | -2.40970 |
| H | -3.55342 | 4.77078 | -1.37148 |
| N | -0.07330 | 1.07257 | 0.26811 |
| O | -2.04295 | 1.12114 | 2.54245 |
| C | -2.73612 | 1.23848 | 1.52507 |
| C | -3.90782 | 0.43138 | 1.26825 |
| H | -3.38664 | -0.59828 | 0.72138 |
| H | -4.39136 | 0.07605 | 2.17818 |
| H | -4.60315 | 0.83977 | 0.53796 |
| I | 4.17699 | 0.54999 | -0.15087 |
| O | -2.76116 | -1.74831 | 0.21635 |
| C | -3.38657 | -2.11611 | -0.97883 |
| C | -2.77525 | -3.42069 | -1.50931 |
| H | -2.88027 | -4.21045 | -0.75989 |
| H | -3.26822 | -3.74826 | -2.43018 |
| H | -1.71098 | -3.28776 | -1.72236 |
| C | -3.19996 | -1.00910 | -2.03310 |
| H | -3.62317 | -0.06843 | -1.66727 |
| H | -2.13290 | -0.84994 | -2.22048 |
| H | -3.68215 | -1.26196 | -2.98262 |
| C | -4.89137 | -2.34181 | -0.74830 |
| H | -5.40106 | -2.64750 | -1.66723 |
| H | -5.03427 | -3.12281 | 0.00422 |
| H | -5.36086 | -1.42456 | -0.38265 |
| K | -1.05640 | -1.34895 | 2.03987 |
| C | 0.76101 | 1.55173 | 1.38251 |
| H | 1.40725 | 2.38303 | 1.06614 |
| H | 0.11915 | 1.87373 | 2.19861 |
| H | 1.40005 | 0.73545 | 1.73123 |

**Prod: 22-K** + HOtBu in DMSO

50

-1593.5939433

| | | | |
|---|---|---|---|
| C | -2.27080 | 3.49962 | -0.73167 |
| C | -1.64921 | 2.28662 | -0.98846 |
| C | -2.24798 | 1.06095 | -0.67673 |
| C | -3.51797 | 1.10670 | -0.09948 |
| C | -4.16290 | 2.31421 | 0.16190 |
| C | -3.53492 | 3.51292 | -0.15133 |
| H | -1.77525 | 4.42734 | -0.99001 |
| H | -0.67166 | 2.27937 | -1.45542 |
| H | -5.14941 | 2.32087 | 0.60737 |
| H | -4.03903 | 4.44972 | 0.05308 |
| C | -1.48532 | -0.20790 | -0.98905 |
| H | -2.16640 | -1.06678 | -0.96372 |
| H | -1.10417 | -0.12462 | -2.00988 |
| C | 0.51475 | -1.48764 | -0.42133 |
| C | 1.72032 | -1.72374 | 0.29658 |
| C | 0.19965 | -2.34233 | -1.48968 |
| C | 2.51995 | -2.80433 | -0.08494 |
| C | 1.02884 | -3.39884 | -1.85482 |
| H | -0.71567 | -2.20687 | -2.04691 |
| C | 2.19413 | -3.64393 | -1.14596 |
| H | 3.44157 | -2.96810 | 0.46211 |
| H | 0.74582 | -4.02960 | -2.68965 |
| H | 2.84747 | -4.46492 | -1.41550 |
| N | -0.34343 | -0.40249 | -0.08534 |
| O | 2.26612 | 0.45388 | 1.12894 |
| C | 2.24438 | -0.81949 | 1.39751 |
| C | 2.66719 | -1.39401 | 2.55485 |
| H | 3.62454 | 1.33034 | 0.70595 |
| H | 3.06485 | -0.77484 | 3.35123 |
| H | 2.60517 | -2.46299 | 2.70894 |
| I | -4.59472 | -0.66257 | 0.43742 |
| O | 4.28746 | 1.84002 | 0.17721 |
| C | 5.53470 | 1.14356 | 0.26039 |
| C | 6.57337 | 2.03257 | -0.40862 |
| H | 6.64465 | 2.98922 | 0.11437 |
| H | 7.55478 | 1.55307 | -0.39494 |
| H | 6.29424 | 2.22350 | -1.44783 |
| C | 5.41411 | -0.19504 | -0.47050 |
| H | 4.62905 | -0.80239 | -0.00963 |
| H | 5.16649 | -0.03164 | -1.52344 |
| H | 6.35232 | -0.75362 | -0.42282 |
| C | 5.88079 | 0.90740 | 1.72987 |
| H | 6.83872 | 0.39032 | 1.82591 |
| H | 5.94324 | 1.86061 | 2.26056 |
| H | 5.10631 | 0.29228 | 2.19902 |
| K | 2.09576 | 1.03017 | -1.38118 |
| C | -0.77263 | -0.39234 | 1.31956 |
| H | -1.49177 | -1.20095 | 1.51114 |
| H | 0.07776 | -0.51070 | 1.98239 |
| H | -1.25027 | 0.56119 | 1.54643 |




18 22-K

**SM: 18** + KOtBu in Benzene

50

-1593.5576446

| | | | |
|---|---|---|---|
| C | -2.54974 | 3.40318 | -0.15063 |
| C | -1.80531 | 2.26837 | -0.42755 |
| C | -2.37556 | 0.99104 | -0.45652 |
| C | -3.74095 | 0.89827 | -0.19202 |
| C | -4.50897 | 2.02866 | 0.08518 |
| C | -3.91221 | 3.28110 | 0.10647 |
| H | -2.07364 | 4.37583 | -0.13499 |
| H | -0.74233 | 2.35568 | -0.62126 |
| H | -5.56733 | 1.92875 | 0.28764 |
| H | -4.51226 | 4.15564 | 0.32710 |
| C | -1.46582 | -0.18031 | -0.76168 |
| H | -2.04916 | -1.10132 | -0.86902 |
| H | -0.97655 | 0.01461 | -1.71969 |
| C | 0.64344 | -1.16317 | -0.00872 |
| C | 1.76834 | -1.23789 | 0.86201 |
| C | 0.65300 | -1.97117 | -1.16010 |
| C | 2.77711 | -2.17114 | 0.59605 |
| C | 1.69638 | -2.84960 | -1.41812 |
| H | -0.18215 | -1.95176 | -1.84569 |
| C | 2.75797 | -2.97612 | -0.53046 |
| H | 3.62637 | -2.22877 | 1.26421 |
| H | 1.65998 | -3.45972 | -2.31347 |
| H | 3.56538 | -3.67045 | -0.72268 |
| N | -0.43405 | -0.31916 | 0.26513 |
| O | 1.54648 | 0.87692 | 1.90758 |
| C | 2.03859 | -0.23843 | 1.93967 |
| C | 3.00658 | -0.59585 | 3.04061 |
| H | 4.02615 | -0.47985 | 2.66086 |
| H | 2.86345 | 0.10491 | 3.86062 |
| H | 2.87909 | -1.62187 | 3.38636 |
| I | -4.78036 | -0.96922 | -0.16727 |
| O | 4.40796 | 0.96307 | -0.55328 |
| C | 5.73205 | 0.60414 | -0.59992 |
| C | 6.62255 | 1.83675 | -0.86152 |
| H | 6.47144 | 2.57126 | -0.06473 |
| H | 7.68825 | 1.58606 | -0.90786 |
| H | 6.33191 | 2.29856 | -1.80991 |
| C | 5.98036 | -0.42105 | -1.72610 |
| H | 5.35998 | -1.30597 | -1.55251 |
| H | 5.68893 | 0.01596 | -2.68603 |
| H | 7.02869 | -0.73416 | -1.78900 |
| C | 6.17414 | -0.03293 | 0.73418 |
| H | 7.23559 | -0.30496 | 0.74349 |
| H | 5.98698 | 0.67147 | 1.55104 |
| H | 5.58573 | -0.93878 | 0.91447 |
| K | 2.16406 | 1.60730 | -0.62799 |
| C | -0.97459 | -0.30612 | 1.62998 |
| H | -0.36857 | -0.93277 | 2.28081 |
| H | -0.99513 | 0.70454 | 2.03950 |
| H | -1.99027 | -0.71539 | 1.62267 |

**TS: 18** + KOtBu in Benzene

50

-1593.5552182

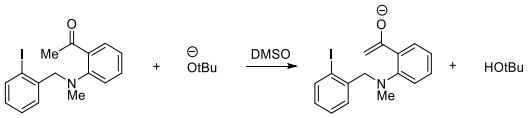
| | | | |
|---|---|---|---|
| C | -1.65606 | 2.60591 | -1.07301 |
| C | -1.43338 | 1.57154 | -0.17305 |
| C | -2.44757 | 0.66658 | 0.15546 |
| C | -3.68923 | 0.84563 | -0.45182 |
| C | -3.92832 | 1.87265 | -1.35876 |
| C | -2.90204 | 2.75591 | -1.67227 |
| H | -0.85281 | 3.29300 | -1.31131 |
| H | -0.45850 | 1.44433 | 0.28949 |
| H | -4.90366 | 1.98239 | -1.81554 |
| H | -3.08213 | 3.55452 | -2.38193 |
| C | -2.17852 | -0.44037 | 1.16297 |
| H | -2.62355 | -0.15062 | 2.11855 |
| H | -2.69939 | -1.35368 | 0.85695 |
| C | 0.01054 | -1.18241 | 0.35825 |
| C | 1.42300 | -1.08470 | 0.37302 |
| C | -0.58743 | -1.81778 | -0.74902 |
| C | 2.17414 | -1.72812 | -0.61354 |
| C | 0.18176 | -2.41207 | -1.73827 |
| H | -1.66508 | -1.86310 | -0.83577 |
| C | 1.57173 | -2.39865 | -1.66891 |
| H | 3.25403 | -1.63429 | -0.57485 |
| H | -0.31772 | -2.90014 | -2.56772 |
| H | 2.17236 | -2.86989 | -2.43688 |
| N | -0.77197 | -0.68529 | 1.38764 |
| O | 1.74565 | 1.02219 | 1.38151 |
| C | 2.16974 | -0.14311 | 1.27464 |
| C | 3.44096 | -0.56102 | 1.81865 |
| H | 4.27012 | -0.16632 | 0.89209 |
| H | 3.72439 | 0.01185 | 2.70173 |
| H | 3.55952 | -1.63478 | 1.94588 |
| I | -5.33155 | -0.44475 | 0.00859 |
| O | 5.01080 | 0.46748 | -0.04300 |
| C | 6.07983 | -0.23746 | -0.60547 |
| C | 7.35383 | 0.61404 | -0.51141 |
| H | 7.57831 | 0.82830 | 0.53724 |
| H | 8.21684 | 0.10982 | -0.95729 |
| H | 7.20175 | 1.56393 | -1.03242 |
| C | 5.78396 | -0.53568 | -2.08254 |
| H | 4.87603 | -1.13917 | -2.16955 |
| H | 5.62053 | 0.40155 | -2.62192 |
| H | 6.60651 | -1.07456 | -2.56301 |
| C | 6.31061 | -1.56107 | 0.14120 |
| H | 7.16307 | -2.10635 | -0.27357 |
| H | 6.50407 | -1.36518 | 1.19983 |
| H | 5.42735 | -2.20287 | 0.07169 |
| K | 3.70736 | 2.50122 | 0.45961 |
| C | -0.28186 | -0.53790 | 2.74678 |
| H | 0.61682 | -1.14101 | 2.88485 |
| H | -0.03944 | 0.49960 | 2.99559 |
| H | -1.03893 | -0.91032 | 3.44114 |

**Prod: 22-K** + HOtBu in Benzene

50

-1593.5770718

| | | | |
|---|---|---|---|
| C | -2.26058 | 3.49055 | -0.76041 |
| C | -1.64600 | 2.27391 | -1.01378 |
| C | -2.24464 | 1.05193 | -0.69046 |
| C | -3.51175 | 1.10290 | -0.10772 |
| C | -4.14960 | 2.31470 | 0.15060 |
| C | -3.52022 | 3.50970 | -0.17138 |
| H | -1.76426 | 4.41593 | -1.02551 |
| H | -0.67176 | 2.25959 | -1.48928 |
| H | -5.13309 | 2.32563 | 0.60246 |
| H | -4.01938 | 4.44909 | 0.03301 |
| C | -1.48322 | -0.21905 | -0.99574 |
| H | -2.16397 | -1.07830 | -0.96849 |
| H | -1.10455 | -0.13933 | -2.01874 |
| C | 0.52077 | -1.49416 | -0.43249 |
| C | 1.72021 | -1.73779 | 0.29389 |
| C | 0.21869 | -2.33122 | -1.51831 |
| C | 2.53267 | -2.80106 | -0.10692 |
| C | 1.05896 | -3.37409 | -1.89834 |
| H | -0.69893 | -2.19955 | -2.07285 |
| C | 2.22221 | -3.62059 | -1.18811 |
| H | 3.44949 | -2.96738 | 0.44700 |
| H | 0.78429 | -3.99415 | -2.74394 |
| H | 2.88415 | -4.43081 | -1.46882 |
| N | -0.34032 | -0.40878 | -0.09356 |
| O | 2.26130 | 0.42054 | 1.17270 |
| C | 2.22909 | -0.85756 | 1.42188 |
| C | 2.63170 | -1.45647 | 2.57043 |
| H | 3.63838 | 1.26062 | 0.69995 |
| H | 3.01475 | -0.85260 | 3.38476 |
| H | 2.55708 | -2.52725 | 2.70358 |
| I | -4.58982 | -0.65876 | 0.43955 |
| O | 4.25099 | 1.72653 | 0.07608 |
| C | 5.55229 | 1.15651 | 0.22768 |
| C | 6.45496 | 1.87800 | -0.76336 |
| H | 6.46935 | 2.94881 | -0.54793 |
| H | 7.47624 | 1.49507 | -0.70421 |
| H | 6.08796 | 1.73334 | -1.78275 |
| C | 5.48728 | -0.34054 | -0.08088 |
| H | 4.81433 | -0.84068 | 0.62250 |
| H | 5.11540 | -0.50220 | -1.09743 |
| H | 6.47604 | -0.79993 | 0.00008 |
| C | 6.03069 | 1.37779 | 1.66199 |
| H | 7.02950 | 0.95956 | 1.81047 |
| H | 6.05905 | 2.44623 | 1.88738 |
| H | 5.34560 | 0.89202 | 2.36307 |
| K | 2.00501 | 1.03643 | -1.25044 |
| C | -0.76828 | -0.39148 | 1.31385 |
| H | 0.08301 | -0.49975 | 1.97652 |
| H | -1.24735 | 0.56287 | 1.53283 |
| H | -1.48357 | -1.20192 | 1.50857 |




18 22

**SM: 18** + tert-butoxide anion in DMSO

49

-993.6862317

| | | | |
|---|---|---|---|
| C | 2.33914 | 2.46998 | 1.85356 |
| C | 1.75622 | 1.83461 | 0.76374 |
| C | 2.41549 | 0.80401 | 0.08575 |
| C | 3.68118 | 0.44171 | 0.54461 |
| C | 4.27956 | 1.06421 | 1.63495 |
| C | 3.60078 | 2.08374 | 2.29375 |
| H | 1.80655 | 3.26609 | 2.36027 |
| H | 0.76943 | 2.12979 | 0.41966 |
| H | 5.26366 | 0.75989 | 1.96750 |
| H | 4.06233 | 2.56945 | 3.14507 |
| C | 1.76844 | 0.14749 | -1.12315 |
| H | 2.25046 | 0.53688 | -2.02291 |
| H | 1.97198 | -0.92830 | -1.11678 |
| C | -0.51814 | -0.13389 | -0.30583 |
| C | -1.86457 | 0.30242 | -0.18135 |
| C | -0.09063 | -1.17236 | 0.54900 |
| C | -2.76077 | -0.40320 | 0.63216 |
| C | -0.98333 | -1.81973 | 1.38952 |
| H | 0.94206 | -1.49462 | 0.54710 |
| C | -2.33026 | -1.46685 | 1.41539 |
| H | -3.80202 | -0.07838 | 0.69354 |
| H | -0.61785 | -2.62100 | 2.02237 |
| H | -3.02546 | -1.98788 | 2.06241 |
| N | 0.34910 | 0.40655 | -1.23496 |
| O | -1.60913 | 2.61075 | -0.58995 |
| C | -2.32974 | 1.63169 | -0.69042 |
| C | -3.71104 | 1.72466 | -1.27256 |
| H | -4.47482 | 1.35272 | -0.57114 |
| H | -3.91743 | 2.75680 | -1.55426 |
| H | -3.76312 | 1.08159 | -2.15723 |
| I | 4.80154 | -1.09634 | -0.43297 |
| O | -5.91168 | 0.51514 | 0.76085 |
| C | -6.56818 | -0.57783 | 0.24576 |
| C | -8.09575 | -0.35044 | 0.20463 |
| H | -8.31780 | 0.53306 | -0.40271 |
| H | -8.63964 | -1.20478 | -0.21523 |
| H | -8.46839 | -0.16862 | 1.21782 |
| C | -6.30100 | -1.84097 | 1.09636 |
| H | -5.22722 | -2.05227 | 1.10621 |
| H | -6.62401 | -1.66386 | 2.12730 |
| H | -6.82277 | -2.72714 | 0.71670 |
| C | -6.09948 | -0.88432 | -1.19708 |
| H | -6.60267 | -1.75935 | -1.62411 |
| H | -6.29779 | -0.02206 | -1.84203 |
| H | -5.01999 | -1.06760 | -1.20239 |
| C | -0.10719 | 1.05054 | -2.45534 |
| H | -1.13234 | 0.74784 | -2.67594 |
| H | -0.07583 | 2.14188 | -2.39148 |
| H | 0.51962 | 0.72013 | -3.28549 |

**TS: 18** + tert-butoxide anion in DMSO

49

-993.6790290

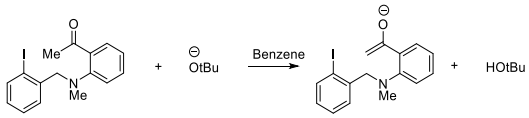
| | | | |
|---|---|---|---|
| C | -1.91139 | 2.79450 | -1.14290 |
| C | -1.46672 | 1.79217 | -0.28820 |
| C | -2.30829 | 0.74415 | 0.09873 |
| C | -3.60986 | 0.74908 | -0.40142 |
| C | -4.07205 | 1.74226 | -1.25763 |
| C | -3.21285 | 2.76987 | -1.63266 |
| H | -1.23911 | 3.59520 | -1.42759 |
| H | -0.45040 | 1.81041 | 0.09589 |
| H | -5.08920 | 1.71773 | -1.62711 |
| H | -3.56691 | 3.54445 | -2.30234 |
| C | -1.80988 | -0.32774 | 1.05669 |
| H | -2.28362 | -0.16673 | 2.02815 |
| H | -2.15523 | -1.31069 | 0.72064 |
| C | 0.46551 | -0.68227 | 0.21932 |
| C | 1.83985 | -0.33557 | 0.20550 |
| C | -0.02635 | -1.43609 | -0.86647 |
| C | 2.68019 | -0.86470 | -0.77652 |
| C | 0.82309 | -1.91598 | -1.85427 |
| H | -1.08048 | -1.66873 | -0.93743 |
| C | 2.19062 | -1.66200 | -1.80509 |
| H | 3.72822 | -0.57883 | -0.75377 |
| H | 0.40480 | -2.50324 | -2.66431 |
| H | 2.85573 | -2.04444 | -2.56997 |
| N | -0.37889 | -0.31640 | 1.25535 |
| O | 1.83633 | 1.83584 | 1.11535 |
| C | 2.42427 | 0.74999 | 1.07955 |
| C | 3.70560 | 0.49194 | 1.70893 |
| H | 4.61122 | 0.66966 | 0.80870 |
| H | 3.91808 | 1.19979 | 2.51063 |
| H | 3.83257 | -0.54586 | 2.01772 |
| I | -4.99780 | -0.78062 | 0.15849 |
| O | 5.55377 | 0.92030 | -0.14672 |
| C | 6.59466 | 0.00496 | -0.28875 |
| C | 7.93952 | 0.68125 | 0.02786 |
| H | 7.93408 | 1.04985 | 1.05788 |
| H | 8.78473 | -0.00510 | -0.09058 |
| H | 8.08940 | 1.53441 | -0.64034 |
| C | 6.63692 | -0.51903 | -1.73483 |
| H | 5.69433 | -1.01903 | -1.97820 |
| H | 6.76743 | 0.31831 | -2.42661 |
| H | 7.45483 | -1.23005 | -1.89201 |
| C | 6.42009 | -1.19675 | 0.66036 |
| H | 7.23712 | -1.91576 | 0.54600 |
| H | 6.39956 | -0.85815 | 1.70070 |
| H | 5.47634 | -1.71161 | 0.45543 |
| C | 0.09941 | -0.00191 | 2.59069 |
| H | 1.09046 | -0.43188 | 2.74106 |
| H | 0.15992 | 1.07488 | 2.77524 |
| H | -0.57322 | -0.45479 | 3.32231 |

**Prod: 22** + HOtBu in DMSO

49

-993.7021697

| | | | |
|---|---|---|---|
| C | -1.38499 | 2.87009 | -0.26495 |
| C | -1.14969 | 1.63088 | 0.31897 |
| C | -2.15447 | 0.65805 | 0.37884 |
| C | -3.39483 | 0.98249 | -0.16699 |
| C | -3.64715 | 2.21673 | -0.75833 |
| C | -2.63164 | 3.16530 | -0.80786 |
| H | -0.59037 | 3.60647 | -0.29927 |
| H | -0.17189 | 1.39514 | 0.73643 |
| H | -4.62233 | 2.43693 | -1.17433 |
| H | -2.82051 | 4.12729 | -1.26950 |
| C | -1.87105 | -0.67656 | 1.05336 |
| H | -2.31562 | -0.65687 | 2.05238 |
| H | -2.38870 | -1.47832 | 0.51795 |
| C | 0.33199 | -1.13604 | 0.07769 |
| C | 1.73413 | -0.91384 | 0.08669 |
| C | -0.26557 | -1.54343 | -1.13258 |
| C | 2.46950 | -1.21946 | -1.06035 |
| C | 0.49253 | -1.81141 | -2.26535 |
| H | -1.33877 | -1.67317 | -1.19081 |
| C | 1.87573 | -1.67810 | -2.23319 |
| H | 3.53913 | -1.04144 | -1.03638 |
| H | -0.00843 | -2.13275 | -3.17197 |
| H | 2.47674 | -1.89119 | -3.10927 |
| N | -0.46319 | -0.96164 | 1.20478 |
| O | 1.95511 | 0.96015 | 1.51799 |
| C | 2.44855 | -0.17778 | 1.21040 |
| C | 3.58174 | -0.75236 | 1.74175 |
| H | 4.68669 | 0.48310 | 0.41186 |
| H | 4.11537 | -0.25252 | 2.54439 |
| H | 3.89921 | -1.74435 | 1.44489 |
| I | -5.02220 | -0.40798 | -0.09598 |
| O | 5.22379 | 1.07525 | -0.15207 |
| C | 6.52089 | 0.49361 | -0.30644 |
| C | 7.17671 | 0.32686 | 1.06473 |
| H | 6.58155 | -0.34555 | 1.68852 |
| H | 8.18163 | -0.09152 | 0.96594 |
| H | 7.24860 | 1.29473 | 1.56694 |
| C | 7.31767 | 1.46551 | -1.16651 |
| H | 6.82934 | 1.60095 | -2.13449 |
| H | 7.38776 | 2.43725 | -0.67195 |
| H | 8.32821 | 1.08679 | -1.33586 |
| C | 6.39781 | -0.86225 | -1.00298 |
| H | 7.38270 | -1.30975 | -1.15906 |
| H | 5.80109 | -1.54749 | -0.39378 |
| H | 5.91057 | -0.74346 | -1.97437 |
| C | 0.04328 | -1.06591 | 2.56145 |
| H | 0.99553 | -1.59267 | 2.56120 |
| H | 0.19806 | -0.08656 | 3.02502 |
| H | -0.66482 | -1.64424 | 3.16121 |




18 22

**SM: 18** + tert-butoxide anion in Benzene

49

-993.6470894

| | | | |
|---|---|---|---|
| C | 2.18800 | 2.36083 | 1.94923 |
| C | 1.65847 | 1.75276 | 0.81794 |
| C | 2.37702 | 0.77880 | 0.11645 |
| C | 3.64347 | 0.44982 | 0.59492 |
| C | 4.18968 | 1.04551 | 1.72601 |
| C | 3.45187 | 2.00614 | 2.40834 |
| H | 1.60754 | 3.10948 | 2.47492 |
| H | 0.66921 | 2.02475 | 0.46012 |
| H | 5.17622 | 0.76374 | 2.07090 |
| H | 3.86901 | 2.47010 | 3.29418 |
| C | 1.78564 | 0.14380 | -1.13272 |
| H | 2.28527 | 0.57802 | -2.00273 |
| H | 2.02765 | -0.92517 | -1.15214 |
| C | -0.51497 | -0.20981 | -0.37613 |
| C | -1.85589 | 0.23421 | -0.24802 |
| C | -0.09769 | -1.27669 | 0.44150 |
| C | -2.76263 | -0.48030 | 0.54383 |
| C | -0.99956 | -1.93744 | 1.26494 |
| H | 0.93235 | -1.60819 | 0.42927 |
| C | -2.33981 | -1.56896 | 1.29853 |
| H | -3.80539 | -0.14561 | 0.61359 |
| H | -0.64395 | -2.75985 | 1.87656 |
| H | -3.04460 | -2.09511 | 1.93109 |
| N | 0.36780 | 0.36592 | -1.28042 |
| O | -1.55933 | 2.54035 | -0.64558 |
| C | -2.30639 | 1.58020 | -0.73550 |
| C | -3.69871 | 1.70454 | -1.27887 |
| H | -4.45898 | 1.37912 | -0.54258 |
| H | -3.87400 | 2.73477 | -1.58715 |
| H | -3.80655 | 1.03155 | -2.13626 |
| I | 4.85163 | -1.00145 | -0.41567 |
| O | -5.73468 | 0.47561 | 0.74287 |
| C | -6.54559 | -0.52027 | 0.28036 |
| C | -8.03912 | -0.14840 | 0.43825 |
| H | -8.24215 | 0.77216 | -0.11780 |
| H | -8.71716 | -0.93290 | 0.07887 |
| H | -8.25037 | 0.04203 | 1.49513 |
| C | -6.30509 | -1.84157 | 1.05299 |
| H | -5.26539 | -2.15575 | 0.91684 |
| H | -6.47106 | -1.66548 | 2.12026 |
| H | -6.96011 | -2.65802 | 0.72371 |
| C | -6.28363 | -0.80426 | -1.22117 |
| H | -6.91911 | -1.60321 | -1.62287 |
| H | -6.46198 | 0.10925 | -1.79814 |
| H | -5.23477 | -1.08988 | -1.35782 |
| C | -0.07531 | 0.99447 | -2.51151 |
| H | -1.09970 | 0.69195 | -2.73434 |
| H | -0.04638 | 2.08682 | -2.45912 |
| H | 0.55673 | 0.65290 | -3.33549 |

**TS: 18** + tert-butoxide anion in Benzene

49

-993.6422758

| | | | |
|---|---|---|---|
| C | -1.87745 | 2.72660 | -1.21736 |
| C | -1.43370 | 1.73532 | -0.34971 |
| C | -2.28543 | 0.70512 | 0.06303 |
| C | -3.59238 | 0.72330 | -0.42039 |
| C | -4.05411 | 1.70475 | -1.28876 |
| C | -3.18374 | 2.71132 | -1.69337 |
| H | -1.19514 | 3.51094 | -1.52270 |
| H | -0.41213 | 1.75690 | 0.02263 |
| H | -5.07667 | 1.68646 | -1.64333 |
| H | -3.53380 | 3.47800 | -2.37453 |
| C | -1.79127 | -0.36733 | 1.02418 |
| H | -2.27780 | -0.21136 | 1.99081 |
| H | -2.13772 | -1.34681 | 0.67902 |
| C | 0.49759 | -0.70784 | 0.20492 |
| C | 1.84125 | -0.26812 | 0.16017 |
| C | 0.04402 | -1.53499 | -0.84012 |
| C | 2.70173 | -0.75447 | -0.82640 |
| C | 0.90800 | -1.97787 | -1.83291 |
| H | -0.98998 | -1.85203 | -0.87688 |
| C | 2.25001 | -1.61350 | -1.82231 |
| H | 3.72589 | -0.38559 | -0.83347 |
| H | 0.52141 | -2.62111 | -2.61602 |
| H | 2.92628 | -1.96130 | -2.59415 |
| N | -0.36627 | -0.36046 | 1.24104 |
| O | 1.71462 | 1.91789 | 1.01831 |
| C | 2.36417 | 0.87171 | 1.00948 |
| C | 3.65093 | 0.68480 | 1.65908 |
| H | 4.56238 | 0.77581 | 0.77411 |
| H | 3.83989 | 1.45091 | 2.41142 |
| H | 3.77913 | -0.32786 | 2.04553 |
| I | -5.00187 | -0.76816 | 0.19916 |
| O | 5.53294 | 0.88164 | -0.21132 |
| C | 6.56579 | -0.03805 | -0.23345 |
| C | 7.89754 | 0.65002 | 0.12291 |
| H | 7.82399 | 1.08406 | 1.12432 |
| H | 8.74755 | -0.04204 | 0.10033 |
| H | 8.08513 | 1.46166 | -0.58580 |
| C | 6.69001 | -0.64723 | -1.64374 |
| H | 5.75810 | -1.15772 | -1.90623 |
| H | 6.85417 | 0.15340 | -2.37033 |
| H | 7.51423 | -1.36615 | -1.71830 |
| C | 6.32962 | -1.18737 | 0.77000 |
| H | 7.13917 | -1.92430 | 0.73501 |
| H | 6.26444 | -0.79039 | 1.78751 |
| H | 5.38614 | -1.69523 | 0.54509 |
| C | 0.09656 | 0.04478 | 2.55570 |
| H | 1.10921 | -0.32431 | 2.72090 |
| H | 0.10414 | 1.13116 | 2.68954 |
| H | -0.55052 | -0.40925 | 3.31128 |

**Prod: 22** + HOtBu in Benzene

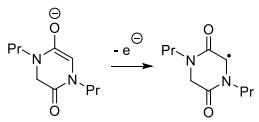
49

-993.6649597

| | | | |
|---|---|---|---|
| C | -1.72628 | 2.64279 | -1.24787 |
| C | -1.33905 | 1.59043 | -0.42457 |
| C | -2.26940 | 0.64153 | 0.00996 |
| C | -3.58993 | 0.80253 | -0.40575 |
| C | -3.99607 | 1.84603 | -1.22794 |
| C | -3.04925 | 2.77222 | -1.65476 |
| H | -0.98301 | 3.36320 | -1.56935 |
| H | -0.30039 | 1.51366 | -0.10249 |
| H | -5.03179 | 1.93757 | -1.52974 |
| H | -3.35387 | 3.58960 | -2.29801 |
| C | -1.84070 | -0.51074 | 0.91102 |
| H | -2.36085 | -0.41144 | 1.86885 |
| H | -2.21250 | -1.44281 | 0.48095 |
| C | 0.46330 | -1.00555 | 0.18623 |
| C | 1.78422 | -0.50948 | 0.05475 |
| C | 0.03967 | -1.99920 | -0.71786 |
| C | 2.61516 | -1.05973 | -0.92416 |
| C | 0.88278 | -2.51169 | -1.69395 |
| H | -0.96096 | -2.40409 | -0.64547 |
| C | 2.19045 | -2.05376 | -1.79892 |
| H | 3.61515 | -0.65081 | -1.02237 |
| H | 0.51017 | -3.27759 | -2.36559 |
| H | 2.85959 | -2.44185 | -2.55799 |
| N | -0.42644 | -0.58560 | 1.18678 |
| O | 1.66255 | 1.78222 | 0.62714 |
| C | 2.31533 | 0.70793 | 0.80440 |
| C | 3.46377 | 0.53806 | 1.55139 |
| H | 4.93060 | 0.88836 | 0.06923 |
| H | 3.86120 | 1.36975 | 2.12434 |
| H | 3.86626 | -0.45384 | 1.71999 |
| I | -5.10557 | -0.57011 | 0.24615 |
| O | 5.69049 | 0.99802 | -0.54066 |
| C | 6.76176 | 0.17395 | -0.09677 |
| C | 7.10240 | 0.49249 | 1.36086 |
| H | 6.25095 | 0.26700 | 2.00755 |
| H | 7.96104 | -0.09612 | 1.69627 |
| H | 7.34159 | 1.55379 | 1.46352 |
| C | 7.94228 | 0.50839 | -1.00157 |
| H | 7.68390 | 0.30469 | -2.04348 |
| H | 8.19438 | 1.56737 | -0.90889 |
| H | 8.81793 | -0.08800 | -0.73281 |
| C | 6.38429 | -1.30248 | -0.24350 |
| H | 7.21636 | -1.94897 | 0.04992 |
| H | 5.52135 | -1.54098 | 0.38349 |
| H | 6.12230 | -1.51787 | -1.28281 |
| C | 0.00590 | 0.10212 | 2.39289 |
| H | 1.02395 | -0.19229 | 2.63987 |
| H | -0.01090 | 1.19266 | 2.29345 |
| H | -0.65019 | -0.20280 | 3.21334 |

## 2. Marcus Theory

### 2.1 Electron Donors



7 8

**SM (Before SET): 7** in DMSO

31

-651.2914030

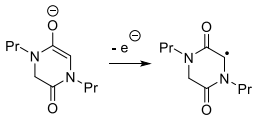
| | | | |
|---|---|---|---|
| C | -0.56308 | 1.32020 | -0.08500 |
| C | 0.94857 | 1.38523 | -0.15358 |
| C | 0.68653 | -0.85826 | -1.02052 |
| C | -0.53159 | -1.07745 | -0.40237 |
| H | -0.95487 | 1.54542 | -1.09451 |
| H | -0.90990 | 2.09445 | 0.60019 |
| H | 1.20260 | -1.64595 | -1.54611 |
| O | -1.22857 | -2.13762 | -0.46120 |
| O | 1.59237 | 2.38782 | 0.20409 |
| N | 1.49463 | 0.27481 | -0.65443 |
| N | -0.99909 | 0.01554 | 0.38634 |
| C | -2.38427 | -0.03585 | 0.83385 |
| H | -2.56466 | -1.03220 | 1.23938 |
| H | -2.49823 | 0.68362 | 1.65295 |
| C | -3.41885 | 0.26076 | -0.25427 |
| H | -3.23822 | -0.41746 | -1.09321 |
| H | -3.28584 | 1.28187 | -0.62565 |
| C | -4.84129 | 0.08958 | 0.27265 |
| H | -5.58392 | 0.30339 | -0.49849 |
| H | -5.00491 | -0.93344 | 0.62248 |
| H | -5.02903 | 0.76281 | 1.11391 |
| C | 2.94718 | 0.18121 | -0.77356 |
| H | 3.16093 | -0.58781 | -1.51969 |
| H | 3.31963 | 1.13584 | -1.14936 |
| C | 3.62809 | -0.15765 | 0.55220 |
| H | 4.70842 | -0.18723 | 0.37822 |
| H | 3.43912 | 0.65910 | 1.25412 |
| C | 3.15542 | -1.48089 | 1.14836 |
| H | 3.67449 | -1.69466 | 2.08508 |
| H | 2.08166 | -1.45355 | 1.34828 |
| H | 3.34336 | -2.30950 | 0.45945 |

**Prod (After SET): 8** in DMSO

31

-651.1622504

| | | | |
|---|---|---|---|
| C | -0.57919 | 1.33192 | 0.04489 |
| C | 0.92606 | 1.35880 | -0.10831 |
| C | 0.76440 | -0.92631 | -0.81097 |
| C | -0.58241 | -1.08563 | -0.31195 |
| H | -0.99785 | 1.77704 | -0.86947 |
| H | -0.82906 | 1.98945 | 0.87778 |
| H | 1.25190 | -1.76322 | -1.28656 |
| O | -1.16876 | -2.17091 | -0.39191 |
| O | 1.57458 | 2.36039 | 0.12621 |
| N | 1.50312 | 0.20889 | -0.59576 |
| N | -1.12745 | 0.01041 | 0.29637 |
| C | -2.50434 | -0.05456 | 0.77456 |
| H | -2.65660 | -1.04504 | 1.20502 |
| H | -2.60914 | 0.68186 | 1.57636 |
| C | -3.53705 | 0.20341 | -0.32197 |
| H | -3.39189 | -0.53448 | -1.11595 |
| H | -3.36823 | 1.19176 | -0.76067 |
| C | -4.95687 | 0.11801 | 0.23111 |
| H | -5.69665 | 0.28986 | -0.55218 |
| H | -5.14633 | -0.86785 | 0.66361 |
| H | -5.11557 | 0.86422 | 1.01395 |
| C | 2.95473 | 0.19775 | -0.83939 |
| H | 3.14456 | -0.58718 | -1.57309 |
| H | 3.22041 | 1.15778 | -1.27998 |
| C | 3.74916 | -0.05130 | 0.44050 |
| H | 4.80882 | -0.01602 | 0.17286 |
| H | 3.56746 | 0.77240 | 1.13528 |
| C | 3.42021 | -1.38725 | 1.10105 |
| H | 4.05101 | -1.54966 | 1.97649 |
| H | 2.37909 | -1.42298 | 1.43192 |
| H | 3.58352 | -2.21796 | 0.40879 |



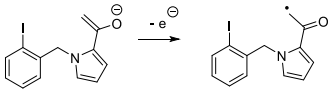

7 8

**SM (Before SET): 7** in Benzene
31
-651.2494131

| | | | |
|---|---|---|---|
| C | 1.09766 | -1.31030 | -1.01114 |
| C | -0.25598 | -1.54171 | -0.85917 |
| C | -0.39270 | -0.68684 | 1.41033 |
| C | 1.06343 | -1.12076 | 1.42370 |
| H | -0.85494 | -1.98727 | -1.63940 |
| H | 1.56546 | -0.62359 | 2.25541 |
| H | 1.07917 | -2.20401 | 1.60368 |
| N | -0.99541 | -1.01576 | 0.26032 |
| N | 1.76928 | -0.85118 | 0.18249 |
| O | -0.93836 | -0.08052 | 2.34605 |
| O | 1.79364 | -1.46834 | -2.05196 |
| C | -2.35834 | -0.56934 | 0.02229 |
| H | -2.83142 | -1.28472 | -0.65784 |
| H | -2.89450 | -0.59066 | 0.97303 |
| C | -2.40342 | 0.83585 | -0.57339 |
| H | -1.93962 | 1.52310 | 0.14088 |
| H | -1.79068 | 0.84585 | -1.47992 |
| C | -3.83166 | 1.27220 | -0.88615 |
| H | -3.85914 | 2.28033 | -1.30489 |
| H | -4.29547 | 0.59608 | -1.61023 |
| H | -4.44853 | 1.26754 | 0.01701 |
| C | 2.40137 | 0.45497 | 0.06179 |
| H | 3.11381 | 0.57947 | 0.88715 |
| H | 2.97722 | 0.44055 | -0.86702 |
| C | 1.42443 | 1.63540 | 0.04331 |
| H | 0.86835 | 1.66706 | 0.98711 |
| H | 0.68986 | 1.46070 | -0.75085 |
| C | 2.14639 | 2.96162 | -0.18039 |
| H | 1.45195 | 3.80468 | -0.18617 |
| H | 2.88324 | 3.14111 | 0.60845 |
| H | 2.67871 | 2.95665 | -1.13573 |

**Prod (After SET): 8** in Benzene
31
-651.1544696

| | | | |
|---|---|---|---|
| C | 0.82862 | 1.18260 | -0.36753 |
| C | -0.61407 | 1.21798 | -0.28654 |
| C | -0.84757 | -1.17041 | -0.37225 |
| C | 0.64396 | -1.24926 | -0.12831 |
| H | -1.11187 | 2.17357 | -0.22355 |
| H | 0.76806 | -1.48490 | 0.93938 |
| H | 1.01085 | -2.10663 | -0.69508 |
| N | -1.39088 | 0.09556 | -0.42397 |
| N | 1.38802 | -0.06302 | -0.50808 |
| O | -1.52852 | -2.17137 | -0.45516 |
| O | 1.49443 | 2.21741 | -0.36392 |
| C | -2.85157 | 0.22859 | -0.49793 |
| H | -3.06657 | 1.17187 | -1.00344 |
| H | -3.22301 | -0.58789 | -1.11716 |
| C | -3.49171 | 0.18724 | 0.88566 |
| H | -3.23177 | -0.76214 | 1.36156 |
| H | -3.06628 | 0.98764 | 1.49874 |
| C | -5.00726 | 0.33700 | 0.79433 |
| H | -5.46295 | 0.30522 | 1.78483 |
| H | -5.28051 | 1.28724 | 0.32856 |
| H | -5.44285 | -0.46843 | 0.19810 |
| C | 2.84221 | -0.17387 | -0.52473 |
| H | 3.09811 | -1.08768 | -1.06986 |
| H | 3.22702 | 0.67608 | -1.08959 |
| C | 3.46396 | -0.19278 | 0.87104 |
| H | 3.07282 | -1.04347 | 1.43815 |
| H | 3.16029 | 0.71724 | 1.39592 |
| C | 4.98569 | -0.27907 | 0.79488 |
| H | 5.43083 | -0.29916 | 1.79079 |
| H | 5.30070 | -1.18380 | 0.26798 |
| H | 5.39616 | 0.58097 | 0.26001 |



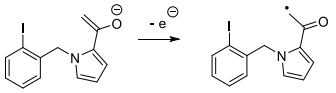
21 S12

**SM (Before SET): 21** in DMSO
27
-643.3534550

| | | | |
|---|---|---|---|
| C | -0.19425 | 3.13096 | 0.61929 |
| C | 0.48823 | 2.02604 | 0.12417 |
| C | -0.17065 | 0.82197 | -0.13440 |
| C | -1.54035 | 0.77040 | 0.12501 |
| C | -2.24063 | 1.86417 | 0.62054 |
| C | -1.56008 | 3.05215 | 0.86780 |
| H | 0.34214 | 4.05208 | 0.81267 |
| H | 1.55519 | 2.08559 | -0.06185 |
| H | -3.30395 | 1.79408 | 0.81225 |
| H | -2.10092 | 3.90756 | 1.25428 |
| C | 0.57985 | -0.38393 | -0.66900 |
| H | 0.45527 | -1.22759 | 0.01110 |
| H | 0.15768 | -0.67123 | -1.63589 |
| N | 1.99662 | -0.15003 | -0.85390 |
| C | 3.03294 | -0.41830 | 0.02340 |
| C | 2.50025 | 0.40213 | -2.00579 |
| C | 4.20111 | -0.03457 | -0.61027 |
| C | 3.86647 | 0.49223 | -1.88521 |
| H | 1.83713 | 0.67086 | -2.81415 |
| H | 5.18521 | -0.13959 | -0.18118 |
| H | 4.54178 | 0.88030 | -2.63237 |
| C | 2.94054 | -1.03489 | 1.39655 |
| C | 1.83748 | -0.79698 | 2.18125 |
| H | 1.03721 | -0.13556 | 1.88257 |
| H | 1.79595 | -1.22761 | 3.17605 |
| O | 3.96816 | -1.72501 | 1.73723 |
| I | -2.63528 | -1.02805 | -0.23517 |

**Prod (After SET): S12** in DMSO
27
-643.1944220

| | | | |
|---|---|---|---|
| C | -0.10861 | 3.13401 | 0.50121 |
| C | 0.54436 | 2.00662 | 0.01592 |
| C | -0.14303 | 0.81040 | -0.19996 |
| C | -1.50863 | 0.78545 | 0.08904 |
| C | -2.17613 | 1.90321 | 0.57491 |
| C | -1.46909 | 3.08363 | 0.78068 |
| H | 0.44724 | 4.04970 | 0.66111 |
| H | 1.60722 | 2.05029 | -0.19666 |
| H | -3.23601 | 1.85761 | 0.79129 |
| H | -1.98626 | 3.95649 | 1.16013 |
| C | 0.56974 | -0.42150 | -0.72668 |
| H | 0.39279 | -1.27847 | -0.07344 |
| H | 0.16320 | -0.69001 | -1.70463 |
| N | 2.00124 | -0.23735 | -0.88326 |
| C | 3.00542 | -0.45767 | 0.04395 |
| C | 2.56253 | 0.21339 | -2.04034 |
| C | 4.20920 | -0.14145 | -0.56504 |
| C | 3.93018 | 0.29294 | -1.87671 |
| H | 1.94042 | 0.43291 | -2.89489 |
| H | 5.17277 | -0.21842 | -0.08626 |
| H | 4.63648 | 0.61868 | -2.62346 |
| C | 2.86543 | -0.94594 | 1.43005 |
| C | 1.65439 | -0.76044 | 2.18891 |
| H | 0.82670 | -0.14877 | 1.86062 |
| H | 1.62121 | -1.20054 | 3.17677 |
| O | 3.84119 | -1.47815 | 1.97467 |
| I | -2.64035 | -0.99922 | -0.20719 |



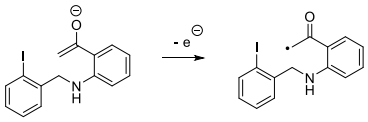
21 S12

**SM (Before SET): 21** in Benzene
27
-643.3105041

| | | | |
|---|---|---|---|
| C | -0.18927 | 3.12100 | 0.58735 |
| C | 0.49230 | 1.99629 | 0.14022 |
| C | -0.17445 | 0.79333 | -0.10569 |
| C | -1.54954 | 0.76710 | 0.12079 |
| C | -2.25060 | 1.88075 | 0.56826 |
| C | -1.56227 | 3.06648 | 0.80074 |
| H | 0.35526 | 4.03859 | 0.77510 |
| H | 1.56565 | 2.03159 | -0.01283 |
| H | -3.31885 | 1.82497 | 0.73552 |
| H | -2.10197 | 3.93845 | 1.15088 |
| C | 0.58125 | -0.43302 | -0.58425 |
| H | 0.50250 | -1.22551 | 0.16299 |
| H | 0.12667 | -0.79352 | -1.51161 |
| N | 1.98102 | -0.18229 | -0.83945 |
| C | 3.05754 | -0.40393 | 0.00198 |
| C | 2.42373 | 0.34838 | -2.02815 |
| C | 4.18879 | -0.01507 | -0.68964 |
| C | 3.79149 | 0.46851 | -1.96399 |
| H | 1.72174 | 0.57987 | -2.81500 |
| H | 5.18798 | -0.09880 | -0.29290 |
| H | 4.42795 | 0.84543 | -2.75009 |
| C | 3.03648 | -0.99100 | 1.39692 |
| C | 1.96210 | -0.72292 | 2.21838 |
| H | 1.16782 | -0.04471 | 1.94020 |
| H | 1.96845 | -1.11297 | 3.22993 |
| O | 4.07214 | -1.66778 | 1.69508 |
| I | -2.65835 | -1.03058 | -0.20895 |

**Prod (After SET): S12** in Benzene
27
-643.1887007

| | | | |
|---|---|---|---|
| C | -0.09337 | 3.12752 | 0.49972 |
| C | 0.55397 | 1.99733 | 0.01438 |
| C | -0.14001 | 0.80482 | -0.20077 |
| C | -1.50532 | 0.78642 | 0.08861 |
| C | -2.16682 | 1.90760 | 0.57447 |
| C | -1.45380 | 3.08400 | 0.77967 |
| H | 0.46716 | 4.04032 | 0.65978 |
| H | 1.61718 | 2.03354 | -0.19857 |
| H | -3.22682 | 1.86604 | 0.79088 |
| H | -1.96607 | 3.95962 | 1.15949 |
| C | 0.56888 | -0.43025 | -0.72579 |
| H | 0.39088 | -1.28381 | -0.06806 |
| H | 0.15659 | -0.70224 | -1.70070 |
| N | 1.99832 | -0.24989 | -0.88728 |
| C | 3.00322 | -0.45798 | 0.04199 |
| C | 2.55850 | 0.20163 | -2.04631 |
| C | 4.20409 | -0.13679 | -0.56590 |
| C | 3.92404 | 0.29032 | -1.88051 |
| H | 1.93564 | 0.41484 | -2.90183 |
| H | 5.16599 | -0.21339 | -0.08417 |
| H | 4.63009 | 0.61443 | -2.62800 |
| C | 2.86689 | -0.94690 | 1.43095 |
| C | 1.65192 | -0.77387 | 2.18989 |
| H | 0.82103 | -0.16275 | 1.86775 |
| H | 1.62766 | -1.21747 | 3.17643 |
| O | 3.84490 | -1.46475 | 1.97641 |
| I | -2.64528 | -0.99255 | -0.20520 |



23 S16

**SM (Before SET): 23** in DMSO

31

-720.7677744

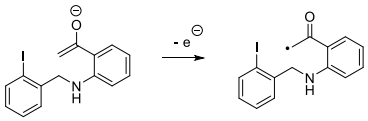
| | | | |
|---|---|---|---|
| C | -1.73558 | 3.23433 | -0.82407 |
| C | -0.74747 | 2.25875 | -0.73798 |
| C | -1.04778 | 0.94259 | -0.37419 |
| C | -2.38964 | 0.64910 | -0.11347 |
| C | -3.39027 | 1.60939 | -0.19452 |
| C | -3.05868 | 2.91335 | -0.55025 |
| H | -1.46657 | 4.24485 | -1.10742 |
| H | 0.27787 | 2.52227 | -0.96792 |
| H | -4.41934 | 1.34660 | 0.01546 |
| H | -3.83591 | 3.66528 | -0.61419 |
| I | -2.98852 | -1.33445 | 0.41192 |
| C | 0.02392 | -0.12112 | -0.28236 |
| H | -0.08088 | -0.64926 | 0.67715 |
| H | -0.18166 | -0.86304 | -1.06129 |
| N | 1.35137 | 0.42235 | -0.44889 |
| C | 2.46684 | -0.40524 | -0.43250 |
| C | 2.40792 | -1.71100 | -0.94701 |
| C | 3.69749 | 0.07171 | 0.09416 |
| C | 3.54359 | -2.51029 | -1.00989 |
| H | 1.46993 | -2.10088 | -1.32247 |
| C | 4.82172 | -0.74858 | -0.00825 |
| C | 4.76634 | -2.02824 | -0.55555 |
| H | 3.46706 | -3.50859 | -1.42643 |
| H | 5.76736 | -0.36774 | 0.36155 |
| H | 5.66056 | -2.63672 | -0.61833 |
| C | 3.78254 | 1.42270 | 0.78244 |
| C | 4.60663 | 1.53105 | 1.87219 |
| H | 4.69386 | 2.48324 | 2.38419 |
| H | 5.16596 | 0.68856 | 2.25480 |
| O | 3.04645 | 2.37249 | 0.30271 |
| H | 1.55686 | 1.31427 | 0.00096 |

**Prod (After SET): S16** in DMSO

31

-720.6100231

| | | | |
|---|---|---|---|
| C | -1.54319 | 3.33997 | -0.42698 |
| C | -0.61671 | 2.30467 | -0.35827 |
| C | -1.01433 | 0.97862 | -0.16525 |
| C | -2.38776 | 0.73624 | -0.06456 |
| C | -3.32712 | 1.75720 | -0.13411 |
| C | -2.90004 | 3.06967 | -0.31095 |
| H | -1.19868 | 4.35617 | -0.57513 |
| H | 0.43509 | 2.53670 | -0.47352 |
| H | -4.38358 | 1.53506 | -0.05376 |
| H | -3.63020 | 3.86810 | -0.36324 |
| I | -3.13409 | -1.25303 | 0.16645 |
| C | -0.01705 | -0.15693 | -0.09442 |
| H | -0.26159 | -0.79600 | 0.76483 |
| H | -0.14527 | -0.77561 | -0.99000 |
| N | 1.34620 | 0.31306 | -0.02654 |
| C | 2.41531 | -0.54215 | -0.08086 |
| C | 2.23525 | -1.91507 | -0.34713 |
| C | 3.74595 | -0.05835 | 0.08961 |
| C | 3.31720 | -2.77410 | -0.43069 |
| H | 1.23755 | -2.31424 | -0.46981 |
| C | 4.81336 | -0.96320 | 0.00908 |
| C | 4.61966 | -2.30944 | -0.24706 |
| H | 3.13888 | -3.82503 | -0.62868 |
| H | 5.82238 | -0.60628 | 0.17352 |
| H | 5.46266 | -2.98617 | -0.29492 |
| C | 4.01330 | 1.37602 | 0.36520 |
| C | 5.32500 | 1.92227 | 0.12086 |
| H | 5.48583 | 2.95793 | 0.38775 |
| H | 6.12050 | 1.37516 | -0.36111 |
| O | 3.12490 | 2.14193 | 0.77685 |
| H | 1.52757 | 1.16565 | 0.48647 |



23 S16

**SM (Before SET): 23** in Benzene

31

-720.7166835

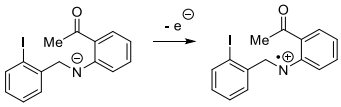
| | | | |
|---|---|---|---|
| C | 1.95348 | 3.49162 | 0.32429 |
| C | 0.84685 | 2.68145 | 0.09345 |
| C | 0.96490 | 1.29622 | -0.05250 |
| C | 2.25147 | 0.76030 | 0.06157 |
| C | 3.36928 | 1.55177 | 0.29358 |
| C | 3.22016 | 2.92943 | 0.42086 |
| H | 1.82198 | 4.56218 | 0.43195 |
| H | -0.14350 | 3.11596 | 0.03528 |
| H | 4.34895 | 1.09873 | 0.37888 |
| H | 4.09062 | 3.54936 | 0.60037 |
| I | 2.55873 | -1.34935 | -0.08140 |
| C | -0.23534 | 0.40943 | -0.30932 |
| H | -0.01426 | -0.28845 | -1.12271 |
| H | -0.39570 | -0.21943 | 0.57205 |
| N | -1.43803 | 1.17381 | -0.55074 |
| C | -2.74099 | 0.72080 | -0.27870 |
| C | -3.75412 | 1.68935 | -0.37674 |
| C | -3.08357 | -0.58863 | 0.11585 |
| C | -5.07693 | 1.39464 | -0.08291 |
| H | -3.47482 | 2.69722 | -0.66998 |
| C | -4.41787 | -0.84662 | 0.44621 |
| C | -5.41660 | 0.11700 | 0.35311 |
| H | -5.83315 | 2.16641 | -0.17796 |
| H | -4.66773 | -1.85817 | 0.74845 |
| H | -6.44308 | -0.12992 | 0.59916 |
| C | -2.11843 | -1.76731 | 0.04919 |
| C | -1.89246 | -2.45649 | 1.21635 |
| H | -1.24235 | -3.32494 | 1.21665 |
| H | -2.36416 | -2.15346 | 2.14264 |
| O | -1.63191 | -1.99588 | -1.10655 |
| H | -1.39316 | 1.75253 | -1.37867 |

**Prod (After SET): S16** in Benzene

31

-720.5944183

| | | | |
|---|---|---|---|
| C | 1.53569 | 3.47701 | 0.44173 |
| C | 0.55526 | 2.54071 | 0.13636 |
| C | 0.86297 | 1.19184 | -0.06249 |
| C | 2.20012 | 0.81645 | 0.09089 |
| C | 3.19431 | 1.73921 | 0.39416 |
| C | 2.86055 | 3.07886 | 0.56221 |
| H | 1.26120 | 4.51461 | 0.58813 |
| H | -0.47822 | 2.86060 | 0.06733 |
| H | 4.22217 | 1.41639 | 0.49929 |
| H | 3.63628 | 3.79911 | 0.79223 |
| I | 2.79632 | -1.22816 | -0.07752 |
| C | -0.21737 | 0.17561 | -0.38039 |
| H | 0.17795 | -0.59634 | -1.04432 |
| H | -0.48123 | -0.33210 | 0.55363 |
| N | -1.40781 | 0.77387 | -0.93953 |
| C | -2.69314 | 0.57644 | -0.49081 |
| C | -3.61927 | 1.62904 | -0.63213 |
| C | -3.13364 | -0.62384 | 0.11133 |
| C | -4.91058 | 1.52049 | -0.15416 |
| H | -3.29171 | 2.54819 | -1.10742 |
| C | -4.43715 | -0.69001 | 0.62419 |
| C | -5.32919 | 0.36035 | 0.50130 |
| H | -5.59401 | 2.35300 | -0.27541 |
| H | -4.76976 | -1.61602 | 1.08136 |
| H | -6.33634 | 0.27450 | 0.88790 |
| C | -2.34417 | -1.89381 | 0.05853 |
| C | -2.40854 | -2.79162 | 1.18598 |
| H | -1.89026 | -3.73820 | 1.11064 |
| H | -2.91311 | -2.52846 | 2.10512 |
| O | -1.66537 | -2.19084 | -0.92545 |
| H | -1.26532 | 1.60653 | -1.48976 |




24 S14

**SM (Before SET): 24** in DMSO

31

-720.7637628

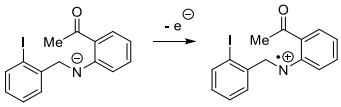
| | | | |
|---|---|---|---|
| C | -2.20085 | 3.46156 | -0.07705 |
| C | -1.04200 | 2.72823 | 0.15431 |
| C | -1.04319 | 1.33020 | 0.16128 |
| C | -2.26927 | 0.70695 | -0.08198 |
| C | -3.44070 | 1.41662 | -0.31935 |
| C | -3.40477 | 2.80811 | -0.31529 |
| H | -2.16245 | 4.54474 | -0.07323 |
| H | -0.09563 | 3.22109 | 0.33673 |
| H | -4.37106 | 0.89531 | -0.50637 |
| H | -4.31436 | 3.36731 | -0.49935 |
| I | -2.41008 | -1.43248 | -0.10797 |
| C | 0.22554 | 0.53757 | 0.41749 |
| H | 0.03072 | -0.15127 | 1.25273 |
| H | 0.38086 | -0.13623 | -0.44661 |
| N | 1.36147 | 1.37618 | 0.64572 |
| C | 2.56248 | 0.92364 | 0.35296 |
| C | 3.64247 | 1.89392 | 0.33478 |
| C | 2.94688 | -0.42694 | -0.04956 |
| C | 4.83261 | 1.64901 | -0.28618 |
| H | 3.43313 | 2.86716 | 0.76734 |
| C | 4.16815 | -0.60837 | -0.75104 |
| C | 5.09689 | 0.39343 | -0.89877 |
| H | 5.58578 | 2.43047 | -0.32256 |
| H | 4.40734 | -1.59716 | -1.12881 |
| H | 6.03183 | 0.21465 | -1.41465 |
| C | 2.27380 | -1.61825 | 0.44272 |
| C | 2.47154 | -2.93961 | -0.28996 |
| H | 1.63342 | -3.59039 | -0.04261 |
| H | 2.53681 | -2.81815 | -1.37121 |
| O | 1.60020 | -1.63374 | 1.47875 |
| H | 3.38859 | -3.42573 | 0.05498 |

**Prod (After SET): S14** in DMSO

31

-720.6061935

| | | | |
|---|---|---|---|
| C | -2.12941 | 3.49306 | -0.16946 |
| C | -0.97564 | 2.74940 | 0.05397 |
| C | -1.01066 | 1.35511 | 0.11108 |
| C | -2.24997 | 0.73664 | -0.06832 |
| C | -3.41335 | 1.46196 | -0.29368 |
| C | -3.34983 | 2.85151 | -0.34378 |
| H | -2.07248 | 4.57432 | -0.20851 |
| H | -0.02134 | 3.24133 | 0.19129 |
| H | -4.35959 | 0.95403 | -0.42997 |
| H | -4.25450 | 3.42069 | -0.52035 |
| I | -2.41311 | -1.39580 | -0.00652 |
| C | 0.24103 | 0.53614 | 0.34971 |
| H | 0.08737 | -0.07883 | 1.24738 |
| H | 0.35016 | -0.17320 | -0.48333 |
| N | 1.40637 | 1.35223 | 0.53191 |
| C | 2.62791 | 0.86578 | 0.27866 |
| C | 3.66250 | 1.85038 | 0.24158 |
| C | 3.00168 | -0.49235 | -0.03143 |
| C | 4.94752 | 1.54813 | -0.15437 |
| H | 3.37825 | 2.86423 | 0.49672 |
| C | 4.29514 | -0.76123 | -0.45133 |
| C | 5.26813 | 0.23989 | -0.52133 |
| H | 5.70128 | 2.32501 | -0.19115 |
| H | 4.57921 | -1.78048 | -0.68675 |
| H | 6.27192 | -0.01047 | -0.84102 |
| C | 2.12566 | -1.67966 | 0.25960 |
| C | 1.89694 | -2.67467 | -0.84549 |
| H | 1.27444 | -3.49045 | -0.48359 |
| H | 1.40960 | -2.17338 | -1.68642 |
| O | 1.65432 | -1.82173 | 1.36781 |
| H | 2.84555 | -3.06760 | -1.21715 |




24 S14

**SM (Before SET): 24** in Benzene

31

-720.7285731

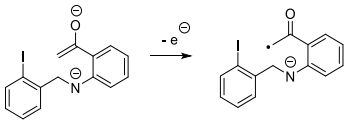
| | | | |
|---|---|---|---|
| C | -2.18980 | 3.45870 | -0.05112 |
| C | -1.03485 | 2.71818 | 0.17078 |
| C | -1.04312 | 1.31980 | 0.16445 |
| C | -2.27245 | 0.70673 | -0.08112 |
| C | -3.44121 | 1.42377 | -0.30962 |
| C | -3.39835 | 2.81440 | -0.29330 |
| H | -2.14542 | 4.54188 | -0.03705 |
| H | -0.08056 | 3.19532 | 0.35661 |
| H | -4.37315 | 0.90612 | -0.49875 |
| H | -4.30555 | 3.38028 | -0.47054 |
| I | -2.42166 | -1.43147 | -0.11951 |
| C | 0.22662 | 0.52742 | 0.41330 |
| H | 0.04317 | -0.15339 | 1.25819 |
| H | 0.37258 | -0.15199 | -0.44832 |
| N | 1.35739 | 1.37496 | 0.62057 |
| C | 2.55791 | 0.92505 | 0.33874 |
| C | 3.62996 | 1.90546 | 0.30819 |
| C | 2.95605 | -0.42924 | -0.04229 |
| C | 4.82307 | 1.66330 | -0.30466 |
| H | 3.40487 | 2.88034 | 0.72814 |
| C | 4.18203 | -0.60738 | -0.73388 |
| C | 5.10250 | 0.39995 | -0.89545 |
| H | 5.56891 | 2.45178 | -0.35078 |
| H | 4.43348 | -1.59961 | -1.09484 |
| H | 6.04137 | 0.22084 | -1.40455 |
| C | 2.28816 | -1.61958 | 0.46027 |
| C | 2.51571 | -2.95171 | -0.25343 |
| H | 1.68206 | -3.60654 | -0.00168 |
| H | 2.58820 | -2.84432 | -1.33619 |
| O | 1.59583 | -1.63596 | 1.47951 |
| H | 3.43603 | -3.41900 | 0.10860 |

**Prod (After SET): S14** in Benzene

31

-720.6004909

| | | | |
|---|---|---|---|
| C | -2.16239 | 3.48716 | -0.12517 |
| C | -1.00117 | 2.75456 | 0.09261 |
| C | -1.02045 | 1.35961 | 0.12702 |
| C | -2.25072 | 0.72902 | -0.06733 |
| C | -3.42124 | 1.44377 | -0.28761 |
| C | -3.37380 | 2.83404 | -0.31626 |
| H | -2.11864 | 4.56948 | -0.14594 |
| H | -0.05248 | 3.25302 | 0.24388 |
| H | -4.35994 | 0.92545 | -0.43572 |
| H | -4.28422 | 3.39538 | -0.48851 |
| I | -2.38905 | -1.40529 | -0.03086 |
| C | 0.23917 | 0.55315 | 0.36408 |
| H | 0.10787 | -0.03901 | 1.28102 |
| H | 0.33676 | -0.17782 | -0.45130 |
| N | 1.40362 | 1.37842 | 0.49932 |
| C | 2.62337 | 0.88238 | 0.25263 |
| C | 3.65652 | 1.86478 | 0.17514 |
| C | 2.99473 | -0.48425 | -0.01455 |
| C | 4.94002 | 1.54965 | -0.21513 |
| H | 3.37086 | 2.88532 | 0.39965 |
| C | 4.28738 | -0.76714 | -0.42861 |
| C | 5.26038 | 0.22943 | -0.53607 |
| H | 5.69339 | 2.32505 | -0.28180 |
| H | 4.56845 | -1.79478 | -0.63001 |
| H | 6.26362 | -0.03178 | -0.84912 |
| C | 2.11738 | -1.66435 | 0.30940 |
| C | 1.86939 | -2.67499 | -0.78078 |
| H | 1.25510 | -3.48532 | -0.39342 |
| H | 1.36128 | -2.18547 | -1.61648 |
| O | 1.66130 | -1.78971 | 1.42247 |
| H | 2.81039 | -3.07126 | -1.16804 |



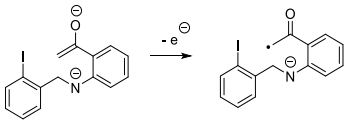
25 43

**SM (Before SET): 25** in DMSO
30
-720.2417849

| | | | |
|---|---|---|---|
| C | -2.13089 | 3.48667 | -0.12209 |
| C | -0.97347 | 2.73231 | 0.04084 |
| C | -0.99777 | 1.33398 | 0.07945 |
| C | -2.25369 | 0.73645 | -0.05454 |
| C | -3.42555 | 1.46515 | -0.22085 |
| C | -3.36283 | 2.85581 | -0.25400 |
| H | -2.07005 | 4.56888 | -0.14653 |
| H | -0.00328 | 3.20129 | 0.14433 |
| H | -4.37746 | 0.95970 | -0.32513 |
| H | -4.27271 | 3.42997 | -0.38273 |
| I | -2.44726 | -1.40102 | -0.02193 |
| C | 0.27881 | 0.53079 | 0.25413 |
| H | 0.11289 | -0.16544 | 1.09151 |
| H | 0.36219 | -0.13072 | -0.62542 |
| N | 1.43073 | 1.36730 | 0.42583 |
| C | 2.64890 | 0.85584 | 0.21220 |
| C | 3.74308 | 1.79505 | 0.21477 |
| C | 3.03607 | -0.51994 | -0.05388 |
| C | 5.03922 | 1.46447 | -0.12249 |
| H | 3.49560 | 2.82383 | 0.46250 |
| C | 4.35689 | -0.80503 | -0.41034 |
| C | 5.37358 | 0.14917 | -0.47220 |
| H | 5.80204 | 2.23874 | -0.11717 |
| H | 4.59688 | -1.84559 | -0.61364 |
| H | 6.38640 | -0.12705 | -0.74045 |
| C | 2.14051 | -1.72034 | 0.19779 |
| C | 1.91602 | -2.60199 | -0.83717 |
| H | 1.34690 | -3.51182 | -0.66687 |
| H | 2.29324 | -2.40793 | -1.83337 |
| O | 1.71046 | -1.86263 | 1.40308 |

**Prod (After SET): 43** in DMSO
30
-720.1128365

| | | | |
|---|---|---|---|
| C | -2.15076 | 3.48302 | -0.05636 |
| C | -0.98080 | 2.73576 | 0.02377 |
| C | -1.00108 | 1.33810 | 0.03484 |
| C | -2.25489 | 0.72718 | -0.04190 |
| C | -3.43696 | 1.45410 | -0.12376 |
| C | -3.38318 | 2.84458 | -0.12967 |
| H | -2.09768 | 4.56537 | -0.06114 |
| H | -0.01740 | 3.22522 | 0.08266 |
| H | -4.39053 | 0.94485 | -0.18241 |
| H | -4.30176 | 3.41570 | -0.19153 |
| I | -2.42678 | -1.40719 | -0.03936 |
| C | 0.27620 | 0.52989 | 0.12722 |
| H | 0.22201 | -0.15568 | 0.98640 |
| H | 0.34337 | -0.14560 | -0.74046 |
| N | 1.43766 | 1.35966 | 0.23231 |
| C | 2.67008 | 0.83590 | 0.12843 |
| C | 3.71419 | 1.81694 | 0.09168 |
| C | 3.05169 | -0.54910 | -0.00725 |
| C | 5.03058 | 1.48485 | -0.12970 |
| H | 3.41283 | 2.85084 | 0.21586 |
| C | 4.39091 | -0.84291 | -0.25004 |
| C | 5.37603 | 0.14142 | -0.32070 |
| H | 5.79022 | 2.25679 | -0.16538 |
| H | 4.67088 | -1.88520 | -0.35732 |
| H | 6.40717 | -0.13723 | -0.50405 |
| C | 2.11159 | -1.71290 | 0.23056 |
| C | 1.91664 | -2.57833 | -0.81433 |
| H | 1.25185 | -3.42858 | -0.70184 |
| H | 2.41462 | -2.42862 | -1.76366 |
| O | 1.60858 | -1.78321 | 1.40823 |



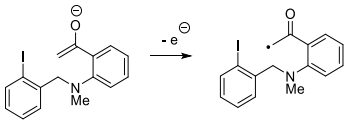
25 43

**SM (Before SET): 25** in Benzene
30
-720.1214667

| | | | |
|---|---|---|---|
| C | -2.13006 | 3.48326 | -0.08063 |
| C | -0.97212 | 2.72390 | 0.04319 |
| C | -1.00023 | 1.32366 | 0.06367 |
| C | -2.26109 | 0.73416 | -0.04657 |
| C | -3.43479 | 1.46873 | -0.17377 |
| C | -3.36913 | 2.85950 | -0.19023 |
| H | -2.06542 | 4.56626 | -0.09175 |
| H | 0.01026 | 3.17310 | 0.12987 |
| H | -4.38871 | 0.96334 | -0.26029 |
| H | -4.28020 | 3.43938 | -0.28789 |
| I | -2.44519 | -1.40246 | -0.03073 |
| C | 0.28209 | 0.52787 | 0.20261 |
| H | 0.15756 | -0.15014 | 1.06378 |
| H | 0.32968 | -0.15607 | -0.66379 |
| N | 1.42583 | 1.38279 | 0.30647 |
| C | 2.64735 | 0.86391 | 0.15422 |
| C | 3.73661 | 1.80906 | 0.13105 |
| C | 3.04676 | -0.52384 | -0.02686 |
| C | 5.04706 | 1.46495 | -0.13021 |
| H | 3.46986 | 2.84834 | 0.30339 |
| C | 4.37986 | -0.82164 | -0.30280 |
| C | 5.40102 | 0.13229 | -0.37588 |
| H | 5.80649 | 2.24427 | -0.14565 |
| H | 4.62515 | -1.87234 | -0.43678 |
| H | 6.42636 | -0.15667 | -0.57852 |
| C | 2.12954 | -1.71806 | 0.21024 |
| C | 1.92439 | -2.59215 | -0.84132 |
| H | 1.32158 | -3.48404 | -0.69331 |
| H | 2.32572 | -2.38895 | -1.82669 |
| O | 1.66406 | -1.84866 | 1.39381 |

**Prod (After SET): 43** in Benzene
30
-720.0741434

| | | | |
|---|---|---|---|
| C | -2.14754 | 3.48074 | -0.06301 |
| C | -0.97917 | 2.73399 | 0.03141 |
| C | -0.99835 | 1.33603 | 0.04211 |
| C | -2.25085 | 0.72442 | -0.04808 |
| C | -3.43154 | 1.45203 | -0.14507 |
| C | -3.37923 | 2.84217 | -0.15177 |
| H | -2.09459 | 4.56345 | -0.06660 |
| H | -0.01300 | 3.21684 | 0.10326 |
| H | -4.38288 | 0.93982 | -0.21424 |
| H | -4.29741 | 3.41316 | -0.22533 |
| I | -2.41074 | -1.40783 | -0.03724 |
| C | 0.27860 | 0.53260 | 0.15251 |
| H | 0.22917 | -0.13937 | 1.02595 |
| H | 0.34475 | -0.17006 | -0.69600 |
| N | 1.43500 | 1.36645 | 0.23497 |
| C | 2.66359 | 0.83819 | 0.13695 |
| C | 3.71468 | 1.81308 | 0.09678 |
| C | 3.03761 | -0.54889 | -0.00061 |
| C | 5.02646 | 1.47353 | -0.13159 |
| H | 3.41696 | 2.84739 | 0.22672 |
| C | 4.37481 | -0.84916 | -0.25811 |
| C | 5.36404 | 0.12707 | -0.33086 |
| H | 5.79124 | 2.24119 | -0.16718 |
| H | 4.64253 | -1.89444 | -0.36874 |
| H | 6.39327 | -0.15638 | -0.52000 |
| C | 2.08785 | -1.70411 | 0.23953 |
| C | 1.91254 | -2.57634 | -0.81073 |
| H | 1.22067 | -3.40579 | -0.71399 |
| H | 2.45058 | -2.44700 | -1.74098 |
| O | 1.54777 | -1.75137 | 1.39115 |



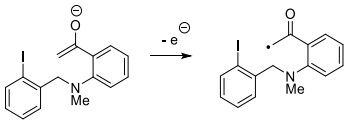
22 S13

**SM (Before SET): 22** in DMSO
34
-760.0540185

| | | | |
|---|---|---|---|
| C | 1.10317 | 2.95839 | -1.21223 |
| C | 0.34944 | 1.81571 | -0.97215 |
| C | 0.93793 | 0.63535 | -0.51100 |
| C | 2.31536 | 0.65403 | -0.29513 |
| C | 3.08908 | 1.78556 | -0.52685 |
| C | 2.47607 | 2.94464 | -0.99176 |
| H | 0.61775 | 3.85860 | -1.56958 |
| H | -0.72282 | 1.82904 | -1.13443 |
| H | 4.15660 | 1.76629 | -0.34843 |
| H | 3.07381 | 3.82903 | -1.17678 |
| I | 3.32002 | -1.08871 | 0.43335 |
| C | 0.09410 | -0.61069 | -0.25803 |
| H | 0.50511 | -1.42861 | -0.86055 |
| H | 0.20993 | -0.91637 | 0.78614 |
| N | -1.30606 | -0.48919 | -0.57416 |
| C | -2.20050 | 0.03460 | 0.35991 |
| C | -1.71345 | 0.76590 | 1.46304 |
| C | -3.59808 | -0.15726 | 0.24979 |
| C | -2.57206 | 1.31749 | 2.40536 |
| H | -0.64908 | 0.93206 | 1.57414 |
| C | -4.43539 | 0.44762 | 1.18760 |
| C | -3.94905 | 1.17864 | 2.26694 |
| H | -2.15581 | 1.87252 | 3.23881 |
| H | -5.50547 | 0.29998 | 1.07479 |
| H | -4.62828 | 1.61458 | 2.98990 |
| C | -4.27713 | -1.02947 | -0.79815 |
| C | -4.09119 | -2.38033 | -0.67816 |
| H | -4.55271 | -3.06408 | -1.38395 |
| H | -3.44126 | -2.78461 | 0.08817 |
| O | -4.99815 | -0.41656 | -1.66733 |
| C | -1.62969 | -0.60499 | -1.98951 |
| H | -1.73882 | -1.64958 | -2.29449 |
| H | -2.56231 | -0.08776 | -2.21003 |
| H | -0.83169 | -0.14374 | -2.58152 |

**Prod (After SET): S13** in DMSO
34
-759.8998739

| | | | |
|---|---|---|---|
| C | 1.14248 | 2.91624 | -1.33950 |
| C | 0.37108 | 1.79676 | -1.05007 |
| C | 0.94193 | 0.62936 | -0.53697 |
| C | 2.31969 | 0.63613 | -0.31735 |
| C | 3.10918 | 1.74492 | -0.59940 |
| C | 2.51446 | 2.89074 | -1.11775 |
| H | 0.67062 | 3.80654 | -1.73701 |
| H | -0.70004 | 1.82583 | -1.21700 |
| H | 4.17574 | 1.71829 | -0.41714 |
| H | 3.12592 | 3.75638 | -1.34224 |
| I | 3.29432 | -1.07795 | 0.50739 |
| C | 0.08912 | -0.59604 | -0.23048 |
| H | 0.49649 | -1.44893 | -0.78369 |
| H | 0.18184 | -0.85065 | 0.82884 |
| N | -1.31177 | -0.48171 | -0.57214 |
| C | -2.20587 | 0.08958 | 0.32519 |
| C | -1.74493 | 0.89855 | 1.38264 |
| C | -3.60192 | -0.10969 | 0.21100 |
| C | -2.63144 | 1.53140 | 2.23983 |
| H | -0.68358 | 1.06756 | 1.51155 |
| C | -4.47650 | 0.58344 | 1.05404 |
| C | -4.00901 | 1.40304 | 2.06846 |
| H | -2.23850 | 2.15218 | 3.03689 |
| H | -5.54048 | 0.42057 | 0.92381 |
| H | -4.69959 | 1.91338 | 2.72760 |
| C | -4.23343 | -1.14224 | -0.67004 |
| C | -3.62101 | -2.44292 | -0.74477 |
| H | -4.11075 | -3.20857 | -1.33188 |
| H | -2.71028 | -2.66973 | -0.20795 |
| O | -5.31294 | -0.92671 | -1.22815 |
| C | -1.60609 | -0.60859 | -1.99643 |
| H | -1.70570 | -1.65413 | -2.30413 |
| H | -2.52581 | -0.07771 | -2.24332 |
| H | -0.79525 | -0.15825 | -2.57631 |




22 S13

**SM (Before SET): 22** in Benzene

34

-760.0128981

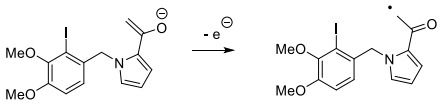
| | | | |
|---|---|---|---|
| C | 1.09738 | 2.96578 | -1.17597 |
| C | 0.34622 | 1.82122 | -0.94106 |
| C | 0.93858 | 0.63743 | -0.49306 |
| C | 2.31605 | 0.65793 | -0.28593 |
| C | 3.08877 | 1.79103 | -0.51229 |
| C | 2.47170 | 2.95270 | -0.96380 |
| H | 0.60754 | 3.86807 | -1.52217 |
| H | -0.72761 | 1.82968 | -1.09364 |
| H | 4.15725 | 1.76895 | -0.33986 |
| H | 3.06700 | 3.83978 | -1.14501 |
| I | 3.32796 | -1.09211 | 0.41862 |
| C | 0.08851 | -0.60794 | -0.24737 |
| H | 0.50220 | -1.42409 | -0.85135 |
| H | 0.20165 | -0.91531 | 0.79705 |
| N | -1.30407 | -0.47543 | -0.57001 |
| C | -2.20638 | 0.03111 | 0.36981 |
| C | -1.72297 | 0.74641 | 1.48373 |
| C | -3.60158 | -0.16744 | 0.25163 |
| C | -2.58537 | 1.26945 | 2.44004 |
| H | -0.65982 | 0.92174 | 1.59618 |
| C | -4.44071 | 0.40528 | 1.20492 |
| C | -3.95935 | 1.11579 | 2.30127 |
| H | -2.17301 | 1.81163 | 3.28422 |
| H | -5.50859 | 0.25093 | 1.08361 |
| H | -4.64240 | 1.52780 | 3.03511 |
| C | -4.27742 | -0.98861 | -0.84479 |
| C | -4.21461 | -2.35012 | -0.69650 |
| H | -4.68783 | -3.00029 | -1.42517 |
| H | -3.69416 | -2.79474 | 0.14299 |
| O | -4.85424 | -0.31951 | -1.76686 |
| C | -1.62784 | -0.61240 | -1.98389 |
| H | -1.74306 | -1.66224 | -2.26946 |
| H | -2.55995 | -0.09832 | -2.21427 |
| H | -0.82479 | -0.16359 | -2.58072 |

**Prod (After SET): S13** in Benzene

34

-759.8943754

| | | | |
|---|---|---|---|
| C | 1.13804 | 2.91243 | -1.34061 |
| C | 0.36775 | 1.79513 | -1.04180 |
| C | 0.94150 | 0.62904 | -0.52940 |
| C | 2.32040 | 0.63509 | -0.31856 |
| C | 3.10845 | 1.74210 | -0.61043 |
| C | 2.51130 | 2.88599 | -1.12893 |
| H | 0.66403 | 3.80217 | -1.73673 |
| H | -0.70504 | 1.82461 | -1.19770 |
| H | 4.17599 | 1.71396 | -0.43463 |
| H | 3.12179 | 3.75036 | -1.36091 |
| I | 3.29821 | -1.07456 | 0.50904 |
| C | 0.08954 | -0.59501 | -0.21379 |
| H | 0.50383 | -1.45180 | -0.75635 |
| H | 0.18008 | -0.83852 | 0.84853 |
| N | -1.31003 | -0.49021 | -0.56056 |
| C | -2.21040 | 0.09260 | 0.32888 |
| C | -1.75636 | 0.91692 | 1.37527 |
| C | -3.60326 | -0.11538 | 0.21037 |
| C | -2.64979 | 1.55444 | 2.22248 |
| H | -0.69633 | 1.09535 | 1.50299 |
| C | -4.48477 | 0.58336 | 1.03958 |
| C | -4.02467 | 1.41644 | 2.04662 |
| H | -2.26352 | 2.18732 | 3.01320 |
| H | -5.54699 | 0.41711 | 0.90039 |
| H | -4.72064 | 1.93232 | 2.69562 |
| C | -4.22785 | -1.15680 | -0.66855 |
| C | -3.61306 | -2.45926 | -0.72668 |
| H | -4.10337 | -3.22849 | -1.30861 |
| H | -2.70661 | -2.68161 | -0.18067 |
| O | -5.29920 | -0.94824 | -1.23700 |
| C | -1.59747 | -0.61240 | -1.98605 |
| H | -1.69112 | -1.65786 | -2.29746 |
| H | -2.52141 | -0.08926 | -2.23391 |
| H | -0.78824 | -0.15478 | -2.56325 |




S1 S15

**SM (Before SET): S1** in DMSO

35

-872.3786917

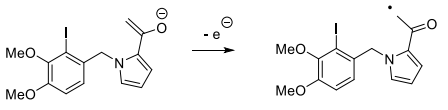
| | | | |
|---|---|---|---|
| C | -1.91698 | 0.82802 | -0.18954 |
| C | -0.95730 | -0.16843 | -0.32191 |
| C | 0.39208 | 0.12040 | -0.55173 |
| C | 0.74493 | 1.46228 | -0.64512 |
| C | -0.19235 | 2.48490 | -0.51601 |
| C | -1.52772 | 2.17678 | -0.28699 |
| H | 0.13290 | 3.51309 | -0.59590 |
| C | 1.42824 | -0.97997 | -0.69660 |
| H | 1.34273 | -1.67609 | 0.13535 |
| H | 1.26609 | -1.52389 | -1.63125 |
| N | 2.78564 | -0.46726 | -0.71240 |
| C | 3.46846 | -0.15929 | -1.86233 |
| C | 3.46148 | 0.03806 | 0.37796 |
| C | 4.61472 | 0.51854 | -1.51768 |
| H | 3.07869 | -0.45706 | -2.82389 |
| C | 4.60953 | 0.64274 | -0.10068 |
| H | 5.37018 | 1.09744 | 0.51568 |
| H | 5.37494 | 0.86331 | -2.20182 |
| C | 2.95968 | -0.12347 | 1.78702 |
| C | 3.18411 | 0.93112 | 2.63689 |
| H | 3.64783 | 1.84399 | 2.28747 |
| H | 2.89139 | 0.85871 | 3.67891 |
| O | 2.37921 | -1.23468 | 2.07293 |
| H | 1.78371 | 1.72167 | -0.81818 |
| O | -3.23265 | 0.52799 | 0.00496 |
| O | -2.52328 | 3.08368 | -0.14482 |
| C | -2.16929 | 4.45827 | -0.21474 |
| H | -3.09328 | 5.01183 | -0.06891 |
| H | -1.45670 | 4.71718 | 0.57258 |
| H | -1.74520 | 4.70241 | -1.19213 |
| C | -3.64465 | 0.64846 | 1.37072 |
| H | -3.06946 | -0.04008 | 1.99596 |
| H | -3.51057 | 1.67441 | 1.71876 |
| H | -4.69868 | 0.38005 | 1.40153 |
| I | -1.63264 | -2.18307 | -0.17108 |

**Prod (After SET): S15** in DMSO

35

-872.2228704

| | | | |
|---|---|---|---|
| C | -1.93018 | 0.81139 | -0.18564 |
| C | -0.96610 | -0.17708 | -0.33980 |
| C | 0.37079 | 0.12706 | -0.61791 |
| C | 0.70494 | 1.46967 | -0.74703 |
| C | -0.23861 | 2.48387 | -0.59757 |
| C | -1.56025 | 2.16363 | -0.31373 |
| H | 0.07134 | 3.51401 | -0.70596 |
| C | 1.41300 | -0.96015 | -0.78857 |
| H | 1.29834 | -1.71350 | -0.01380 |
| H | 1.29479 | -1.44857 | -1.75904 |
| N | 2.77122 | -0.43701 | -0.73964 |
| C | 3.52343 | -0.20168 | -1.84651 |
| C | 3.43985 | 0.04631 | 0.36956 |
| C | 4.69961 | 0.42006 | -1.47116 |
| H | 3.16321 | -0.49672 | -2.82030 |
| C | 4.64719 | 0.57751 | -0.07389 |
| H | 5.41045 | 1.01841 | 0.54746 |
| H | 5.49847 | 0.71520 | -2.13206 |
| C | 2.90260 | -0.02749 | 1.73340 |
| C | 3.69435 | 0.55396 | 2.78919 |
| H | 4.64833 | 1.02873 | 2.61413 |
| H | 3.30386 | 0.50207 | 3.79623 |
| O | 1.81561 | -0.56111 | 1.98890 |
| H | 1.73116 | 1.74311 | -0.96701 |
| O | -3.23403 | 0.49956 | 0.05698 |
| O | -2.55983 | 3.05966 | -0.14595 |
| C | -2.22702 | 4.43800 | -0.24849 |
| H | -3.15214 | 4.98148 | -0.07513 |
| H | -1.48876 | 4.71703 | 0.50768 |
| H | -1.84376 | 4.67292 | -1.24470 |
| C | -3.60446 | 0.63597 | 1.43357 |
| H | -3.00591 | -0.04093 | 2.04936 |
| H | -3.46650 | 1.66728 | 1.76350 |
| H | -4.65518 | 0.36160 | 1.49977 |
| I | -1.61500 | -2.19461 | -0.14443 |




S1 S15

**SM (Before SET): S1** in Benzene

35

-872.3354944

| | | | |
|---|---|---|---|
| C | -1.94488 | 0.84280 | -0.19539 |
| C | -0.99372 | -0.16696 | -0.26785 |
| C | 0.37014 | 0.09720 | -0.42698 |
| C | 0.74922 | 1.43234 | -0.50621 |
| C | -0.17846 | 2.46843 | -0.42933 |
| C | -1.52805 | 2.18264 | -0.27283 |
| H | 0.16959 | 3.49066 | -0.48625 |
| C | 1.39519 | -1.02021 | -0.48772 |
| H | 1.38430 | -1.57867 | 0.44930 |
| H | 1.15657 | -1.69539 | -1.31416 |
| N | 2.74413 | -0.53057 | -0.69210 |
| C | 3.28580 | -0.31500 | -1.93487 |
| C | 3.56030 | 0.01740 | 0.27489 |
| C | 4.48057 | 0.34770 | -1.77566 |
| H | 2.77368 | -0.65922 | -2.82051 |
| C | 4.65393 | 0.55489 | -0.37954 |
| H | 5.49516 | 1.01775 | 0.11279 |
| H | 5.15896 | 0.62460 | -2.56826 |
| C | 3.22070 | -0.04045 | 1.74449 |
| C | 3.62733 | 1.03658 | 2.49537 |
| H | 4.11390 | 1.88880 | 2.03972 |
| H | 3.45416 | 1.03984 | 3.56546 |
| O | 2.59592 | -1.08077 | 2.14812 |
| H | 1.80078 | 1.67308 | -0.61590 |
| O | -3.27549 | 0.56453 | -0.07377 |
| O | -2.51772 | 3.11109 | -0.18109 |
| C | -2.13042 | 4.47174 | -0.21882 |
| H | -3.04791 | 5.04767 | -0.12022 |
| H | -1.45523 | 4.71151 | 0.60782 |
| H | -1.64612 | 4.71706 | -1.16856 |
| C | -3.75468 | 0.68712 | 1.26515 |
| H | -3.21720 | -0.00298 | 1.92210 |
| H | -3.63401 | 1.71283 | 1.62066 |
| H | -4.81088 | 0.42407 | 1.24176 |
| I | -1.70197 | -2.17045 | -0.11463 |

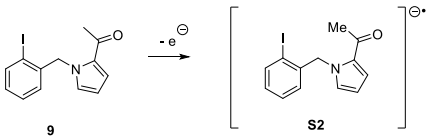
**Prod (After SET): S15** in Benzene

35

-872.2154318

| | | | |
|---|---|---|---|
| C | -1.96077 | 0.81044 | -0.17571 |
| C | -0.99395 | -0.17981 | -0.28768 |
| C | 0.35392 | 0.11937 | -0.51312 |
| C | 0.69962 | 1.45903 | -0.62957 |
| C | -0.24648 | 2.47591 | -0.51659 |
| C | -1.57906 | 2.16079 | -0.28718 |
| H | 0.07121 | 3.50508 | -0.61088 |
| C | 1.38922 | -0.98002 | -0.63614 |
| H | 1.32405 | -1.65050 | 0.21792 |
| H | 1.20965 | -1.56503 | -1.54178 |
| N | 2.74741 | -0.46217 | -0.72764 |
| C | 3.39502 | -0.27588 | -1.90786 |
| C | 3.52494 | 0.04372 | 0.29588 |
| C | 4.60821 | 0.33906 | -1.66698 |
| H | 2.94208 | -0.59918 | -2.83267 |
| C | 4.69114 | 0.53993 | -0.27621 |
| H | 5.51305 | 0.99409 | 0.25405 |
| H | 5.34413 | 0.60022 | -2.40997 |
| C | 3.10476 | 0.03983 | 1.70479 |
| C | 4.03623 | 0.56248 | 2.67602 |
| H | 5.01639 | 0.93034 | 2.41120 |
| H | 3.72505 | 0.56914 | 3.71155 |
| O | 2.00487 | -0.38722 | 2.06520 |
| H | 1.73462 | 1.72795 | -0.80922 |
| O | -3.27309 | 0.50086 | 0.00523 |
| O | -2.58183 | 3.06166 | -0.15800 |
| C | -2.24533 | 4.43391 | -0.27240 |
| H | -3.17624 | 4.98097 | -0.14569 |
| H | -1.53632 | 4.72971 | 0.50604 |
| H | -1.82343 | 4.65223 | -1.25745 |
| C | -3.71426 | 0.64957 | 1.35677 |
| H | -3.13632 | -0.00709 | 2.01338 |
| H | -3.61351 | 1.68813 | 1.67803 |
| H | -4.76182 | 0.35564 | 1.37227 |
| I | -1.65365 | -2.19375 | -0.11221 |

## 2.2 Electron Acceptors



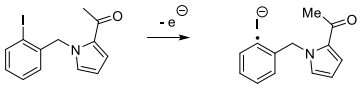

9 S2

**SM (Before SET): 9** in DMSO
28
-643.8557281

| | | | |
|---|---|---|---|
| C | 0.18047 | 3.09141 | 0.31026 |
| C | 0.72224 | 1.91757 | -0.19970 |
| C | -0.05597 | 0.76760 | -0.35478 |
| C | -1.39882 | 0.84048 | 0.01795 |
| C | -1.95619 | 2.00733 | 0.52890 |
| C | -1.15932 | 3.13741 | 0.67688 |
| H | 0.80720 | 3.96787 | 0.42030 |
| H | 1.76920 | 1.88943 | -0.48304 |
| H | -3.00081 | 2.03568 | 0.81181 |
| H | -1.59042 | 4.04645 | 1.07837 |
| C | 0.54449 | -0.50397 | -0.92371 |
| H | 0.20556 | -1.37489 | -0.36709 |
| H | 0.20320 | -0.64297 | -1.95219 |
| N | 1.99817 | -0.47976 | -0.95516 |
| C | 2.88474 | -0.52587 | 0.11295 |
| C | 2.69008 | -0.16022 | -2.08201 |
| C | 4.14855 | -0.24928 | -0.38953 |
| C | 4.02902 | -0.02123 | -1.77226 |
| H | 2.17213 | -0.05099 | -3.02279 |
| H | 5.04855 | -0.24225 | 0.20522 |
| H | 4.81811 | 0.20689 | -2.47062 |
| C | 2.60125 | -0.83247 | 1.52534 |
| C | 1.24508 | -1.32147 | 1.97376 |
| H | 0.96176 | -2.22832 | 1.43507 |
| H | 1.29789 | -1.53773 | 3.03880 |
| O | 3.50071 | -0.70624 | 2.34069 |
| I | -2.67955 | -0.85625 | -0.17130 |
| H | 0.47694 | -0.56326 | 1.80143 |

**Prod (After SET): S2** in DMSO
28
-643.9298114

| | | | |
|---|---|---|---|
| C | 0.35162 | 3.00643 | 0.41367 |
| C | 0.82908 | 1.82249 | -0.13577 |
| C | -0.00778 | 0.71702 | -0.32040 |
| C | -1.33922 | 0.85266 | 0.06812 |
| C | -1.83643 | 2.02848 | 0.62075 |
| C | -0.98173 | 3.11123 | 0.79566 |
| H | 1.02324 | 3.84641 | 0.54479 |
| H | 1.87063 | 1.73919 | -0.42789 |
| H | -2.87646 | 2.10015 | 0.91227 |
| H | -1.36305 | 4.02904 | 1.22705 |
| C | 0.53234 | -0.56336 | -0.93703 |
| H | 0.14328 | -1.42124 | -0.39304 |
| H | 0.15238 | -0.65202 | -1.95944 |
| N | 1.97555 | -0.61415 | -1.00096 |
| C | 2.85130 | -0.57844 | 0.10601 |
| C | 2.64599 | -0.13962 | -2.12744 |
| C | 4.08697 | -0.10265 | -0.39035 |
| C | 3.94013 | 0.15508 | -1.77581 |
| H | 2.13137 | -0.07204 | -3.07366 |
| H | 4.98362 | -0.00315 | 0.20012 |
| H | 4.70606 | 0.50323 | -2.45405 |
| C | 2.55608 | -0.95218 | 1.44758 |
| C | 1.26588 | -1.66110 | 1.82320 |
| H | 0.38139 | -1.01000 | 1.80816 |
| H | 1.05017 | -2.51875 | 1.17578 |
| O | 3.43339 | -0.75799 | 2.37637 |
| I | -2.72160 | -0.76076 | -0.18746 |
| H | 1.38065 | -2.03399 | 2.84198 |



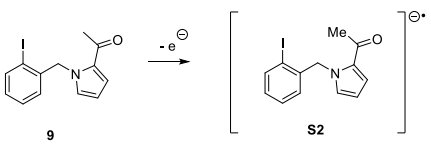

9 S3

**Prod (After SET): S3** in DMSO

28

-643.9665259

| | | | |
|---|---|---|---|
| C | 1.61061 | 3.28725 | 0.44105 |
| C | 1.75340 | 2.03697 | -0.15938 |
| C | 0.62506 | 1.28615 | -0.50875 |
| C | -0.60015 | 1.85200 | -0.22662 |
| C | -0.79512 | 3.07634 | 0.36547 |
| C | 0.34718 | 3.81050 | 0.70463 |
| H | 2.49453 | 3.85420 | 0.70800 |
| H | 2.74541 | 1.63763 | -0.35100 |
| H | -1.78794 | 3.46249 | 0.56816 |
| H | 0.24504 | 4.78188 | 1.17520 |
| C | 0.71973 | -0.07087 | -1.17583 |
| H | -0.08498 | -0.71316 | -0.82199 |
| H | 0.58542 | 0.03802 | -2.25394 |
| N | 2.02036 | -0.70250 | -0.98138 |
| C | 2.59246 | -1.15269 | 0.20008 |
| C | 2.97907 | -0.68168 | -1.94603 |
| C | 3.92543 | -1.43478 | -0.06557 |
| C | 4.17052 | -1.14312 | -1.41973 |
| H | 2.73951 | -0.32978 | -2.93794 |
| H | 4.61727 | -1.83654 | 0.65829 |
| H | 5.09643 | -1.26054 | -1.95958 |
| C | 1.93832 | -1.36633 | 1.50217 |
| C | 0.43726 | -1.34483 | 1.63081 |
| H | 0.03630 | -0.34848 | 1.42834 |
| H | -0.02447 | -2.03378 | 0.92000 |
| O | 2.63630 | -1.60308 | 2.47626 |
| I | -3.21306 | -0.69439 | -0.16554 |
| H | 0.17380 | -1.63667 | 2.64578 |




9 S2

**SM (Before SET): 9** in Benzene

28

-643.8502505

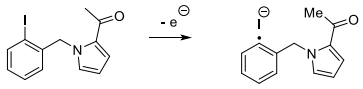
| | | | |
|---|---|---|---|
| C | 0.18553 | 3.08508 | 0.30906 |
| C | 0.72554 | 1.90756 | -0.19354 |
| C | -0.05735 | 0.76107 | -0.34803 |
| C | -1.40133 | 0.84038 | 0.01797 |
| C | -1.95672 | 2.01128 | 0.52064 |
| C | -1.15580 | 3.13829 | 0.66758 |
| H | 0.81598 | 3.95857 | 0.42101 |
| H | 1.77445 | 1.87195 | -0.46882 |
| H | -3.00268 | 2.04373 | 0.79786 |
| H | -1.58485 | 4.05078 | 1.06349 |
| C | 0.54055 | -0.51605 | -0.90721 |
| H | 0.20671 | -1.37893 | -0.33488 |
| H | 0.18626 | -0.66938 | -1.92965 |
| N | 1.99215 | -0.49121 | -0.95504 |
| C | 2.88893 | -0.52629 | 0.10465 |
| C | 2.67241 | -0.16776 | -2.09006 |
| C | 4.14440 | -0.24168 | -0.40849 |
| C | 4.01111 | -0.01726 | -1.79172 |
| H | 2.14529 | -0.06563 | -3.02648 |
| H | 5.04645 | -0.22608 | 0.18266 |
| H | 4.79300 | 0.21415 | -2.49688 |
| C | 2.62205 | -0.82680 | 1.52550 |
| C | 1.26975 | -1.31788 | 1.99055 |
| H | 0.98426 | -2.23013 | 1.46178 |
| H | 1.33850 | -1.52641 | 3.05622 |
| O | 3.52730 | -0.69384 | 2.32685 |
| I | -2.68486 | -0.85414 | -0.16717 |
| H | 0.49659 | -0.56373 | 1.82254 |

**Prod (After SET): S2** in Benzene

28

-643.8897792

| | | | |
|---|---|---|---|
| C | 0.38728 | 2.98132 | 0.27210 |
| C | 0.84948 | 1.75579 | -0.19225 |
| C | -0.00954 | 0.65831 | -0.31550 |
| C | -1.34192 | 0.85102 | 0.03804 |
| C | -1.82666 | 2.06910 | 0.50071 |
| C | -0.94924 | 3.14059 | 0.62256 |
| H | 1.07741 | 3.81134 | 0.36522 |
| H | 1.89347 | 1.63156 | -0.45993 |
| H | -2.87079 | 2.17962 | 0.76357 |
| H | -1.31524 | 4.09221 | 0.99012 |
| C | 0.51077 | -0.67957 | -0.82227 |
| H | 0.14731 | -1.47099 | -0.16846 |
| H | 0.07595 | -0.87241 | -1.80845 |
| N | 1.94480 | -0.74285 | -0.95719 |
| C | 2.87539 | -0.56856 | 0.09778 |
| C | 2.54218 | -0.33592 | -2.15586 |
| C | 4.06149 | -0.08629 | -0.50208 |
| C | 3.83727 | 0.04137 | -1.89170 |
| H | 1.98523 | -0.37843 | -3.07915 |
| H | 4.97332 | 0.10509 | 0.03998 |
| H | 4.55555 | 0.35761 | -2.63507 |
| C | 2.66489 | -0.82043 | 1.48203 |
| C | 1.41465 | -1.53022 | 1.98023 |
| H | 0.51532 | -0.89871 | 1.96559 |
| H | 1.18968 | -2.43921 | 1.40976 |
| O | 3.56047 | -0.50583 | 2.34030 |
| I | -2.75512 | -0.75310 | -0.13405 |
| H | 1.60070 | -1.81605 | 3.01655 |



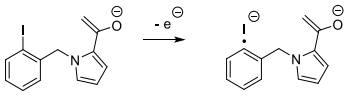

**9** **S3**

**Prod (After SET): S3** in Benzene

28

-643.9288407

| | | | |
|---|---|---|---|
| C | 1.26617 | 3.30715 | 0.52518 |
| C | 1.52459 | 2.08200 | -0.08792 |
| C | 0.46754 | 1.25222 | -0.47816 |
| C | -0.81080 | 1.70704 | -0.22854 |
| C | -1.11079 | 2.90370 | 0.37787 |
| C | -0.04264 | 3.72196 | 0.75930 |
| H | 2.09477 | 3.93655 | 0.82826 |
| H | 2.55015 | 1.76249 | -0.25237 |
| H | -2.13815 | 3.19708 | 0.56385 |
| H | -0.23351 | 4.67305 | 1.24450 |
| C | 0.68077 | -0.08546 | -1.15550 |
| H | -0.05604 | -0.80113 | -0.79415 |
| H | 0.51371 | 0.01391 | -2.23011 |
| N | 2.03961 | -0.59232 | -0.98916 |
| C | 2.66147 | -1.02701 | 0.17030 |
| C | 2.98190 | -0.45412 | -1.96024 |
| C | 4.01074 | -1.17910 | -0.11282 |
| C | 4.21582 | -0.82113 | -1.45825 |
| H | 2.69862 | -0.09610 | -2.93816 |
| H | 4.73801 | -1.53727 | 0.59864 |
| H | 5.14281 | -0.83548 | -2.00888 |
| C | 2.04779 | -1.33503 | 1.47953 |
| C | 0.55202 | -1.40383 | 1.64309 |
| H | 0.08087 | -0.43394 | 1.46402 |
| H | 0.11003 | -2.10911 | 0.93530 |
| O | 2.78585 | -1.56912 | 2.42114 |
| I | -3.07672 | -0.78031 | -0.17658 |
| H | 0.33345 | -1.72506 | 2.65966 |



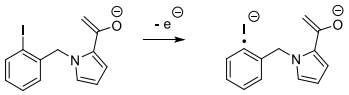
21 S4

**SM (Before SET): 21** in DMSO
27
-643.3534550

| | | | |
|---|---|---|---|
| C | -0.19425 | 3.13096 | 0.61929 |
| C | 0.48823 | 2.02604 | 0.12417 |
| C | -0.17065 | 0.82197 | -0.13440 |
| C | -1.54035 | 0.77040 | 0.12501 |
| C | -2.24063 | 1.86417 | 0.62054 |
| C | -1.56008 | 3.05215 | 0.86780 |
| H | 0.34214 | 4.05208 | 0.81267 |
| H | 1.55519 | 2.08559 | -0.06185 |
| H | -3.30395 | 1.79408 | 0.81225 |
| H | -2.10092 | 3.90756 | 1.25428 |
| C | 0.57985 | -0.38393 | -0.66900 |
| H | 0.45527 | -1.22759 | 0.01110 |
| H | 0.15768 | -0.67123 | -1.63589 |
| N | 1.99662 | -0.15003 | -0.85390 |
| C | 3.03294 | -0.41830 | 0.02340 |
| C | 2.50025 | 0.40213 | -2.00579 |
| C | 4.20111 | -0.03457 | -0.61027 |
| C | 3.86647 | 0.49223 | -1.88521 |
| H | 1.83713 | 0.67086 | -2.81415 |
| H | 5.18521 | -0.13959 | -0.18118 |
| H | 4.54178 | 0.88030 | -2.63237 |
| C | 2.94054 | -1.03489 | 1.39655 |
| C | 1.83748 | -0.79698 | 2.18125 |
| H | 1.03721 | -0.13556 | 1.88257 |
| H | 1.79595 | -1.22761 | 3.17605 |
| O | 3.96816 | -1.72501 | 1.73723 |
| I | -2.63528 | -1.02805 | -0.23517 |

**Prod (After SET): S4** in DMSO
27
-643.4599916

| | | | |
|---|---|---|---|
| C | 1.08996 | 3.43497 | 0.40198 |
| C | 1.44914 | 2.15214 | -0.01206 |
| C | 0.47511 | 1.16324 | -0.18882 |
| C | -0.82665 | 1.53919 | 0.06836 |
| C | -1.23423 | 2.78496 | 0.47838 |
| C | -0.24179 | 3.75810 | 0.64773 |
| H | 1.85916 | 4.18665 | 0.53549 |
| H | 2.49200 | 1.90906 | -0.19347 |
| H | -2.27831 | 3.01125 | 0.66585 |
| H | -0.51257 | 4.75720 | 0.96992 |
| C | 0.80446 | -0.25182 | -0.62616 |
| H | 0.45846 | -0.96029 | 0.12658 |
| H | 0.27681 | -0.47112 | -1.55755 |
| N | 2.22107 | -0.46648 | -0.85392 |
| C | 3.17217 | -0.95319 | 0.02476 |
| C | 2.81692 | -0.16150 | -2.05184 |
| C | 4.37810 | -0.96160 | -0.65432 |
| C | 4.15772 | -0.45302 | -1.96104 |
| H | 2.22595 | 0.22647 | -2.86773 |
| H | 5.30861 | -1.30924 | -0.23302 |
| H | 4.88649 | -0.32488 | -2.74688 |
| C | 2.96378 | -1.41266 | 1.44531 |
| C | 2.01637 | -0.80003 | 2.22917 |
| H | 1.43201 | 0.04278 | 1.89019 |
| H | 1.89377 | -1.12593 | 3.25654 |
| O | 3.75758 | -2.34956 | 1.82339 |
| I | -3.58070 | -0.88515 | -0.13706 |



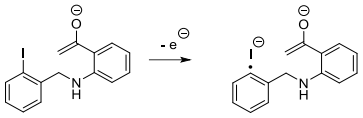
21 S4

**SM (Before SET): 21** in Benzene
27
-643.3105041

| | | | |
|---|---|---|---|
| C | -0.18927 | 3.12100 | 0.58735 |
| C | 0.49230 | 1.99629 | 0.14022 |
| C | -0.17445 | 0.79333 | -0.10569 |
| C | -1.54954 | 0.76710 | 0.12079 |
| C | -2.25060 | 1.88075 | 0.56826 |
| C | -1.56227 | 3.06648 | 0.80074 |
| H | 0.35526 | 4.03859 | 0.77510 |
| H | 1.56565 | 2.03159 | -0.01283 |
| H | -3.31885 | 1.82497 | 0.73552 |
| H | -2.10197 | 3.93845 | 1.15088 |
| C | 0.58125 | -0.43302 | -0.58425 |
| H | 0.50250 | -1.22551 | 0.16299 |
| H | 0.12667 | -0.79352 | -1.51161 |
| N | 1.98102 | -0.18229 | -0.83945 |
| C | 3.05754 | -0.40393 | 0.00198 |
| C | 2.42373 | 0.34838 | -2.02815 |
| C | 4.18879 | -0.01507 | -0.68964 |
| C | 3.79149 | 0.46851 | -1.96399 |
| H | 1.72174 | 0.57987 | -2.81500 |
| H | 5.18798 | -0.09880 | -0.29290 |
| H | 4.42795 | 0.84543 | -2.75009 |
| C | 3.03648 | -0.99100 | 1.39692 |
| C | 1.96210 | -0.72292 | 2.21838 |
| H | 1.16782 | -0.04471 | 1.94020 |
| H | 1.96845 | -1.11297 | 3.22993 |
| O | 4.07214 | -1.66778 | 1.69508 |
| I | -2.65835 | -1.03058 | -0.20895 |

**Prod (After SET): S4** in Benzene
27
-643.3576895

| | | | |
|---|---|---|---|
| C | -0.05400 | -0.27796 | 1.58633 |
| C | 1.17450 | -0.18181 | 0.93511 |
| C | 1.23681 | -0.15230 | -0.46374 |
| C | 0.02585 | -0.22406 | -1.11735 |
| C | -1.21307 | -0.31423 | -0.53243 |
| C | -1.24527 | -0.34148 | 0.86592 |
| H | -0.08071 | -0.29470 | 2.66974 |
| H | 2.09884 | -0.11374 | 1.50196 |
| H | -2.13847 | -0.35037 | -1.09815 |
| H | -2.20625 | -0.40137 | 1.36627 |
| C | 2.54622 | -0.05390 | -1.21916 |
| H | 2.93107 | -1.05034 | -1.44017 |
| H | 2.37170 | 0.46377 | -2.16619 |
| N | 3.57327 | 0.65683 | -0.47574 |
| C | 4.78016 | 0.17099 | -0.00853 |
| C | 3.50839 | 2.01194 | -0.26265 |
| C | 5.47988 | 1.25044 | 0.49589 |
| C | 4.67503 | 2.41127 | 0.34585 |
| H | 2.63594 | 2.56902 | -0.56975 |
| H | 6.46446 | 1.17594 | 0.93009 |
| H | 4.91534 | 3.42032 | 0.64560 |
| C | 5.25247 | -1.26546 | -0.02163 |
| C | 4.32882 | -2.25325 | 0.24150 |
| H | 3.30255 | -2.02865 | 0.50305 |
| H | 4.65231 | -3.28794 | 0.27083 |
| O | 6.50058 | -1.41824 | -0.23247 |
| I | -5.37621 | 0.03708 | -0.04705 |



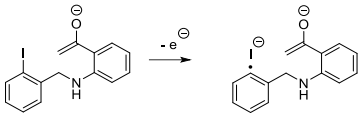
23 S6

**SM (Before SET): 23** in DMSO
31
-720.7677742

| | | | |
|---|---|---|---|
| C | -1.73521 | 3.23425 | -0.82395 |
| C | -0.74727 | 2.25840 | -0.73862 |
| C | -1.04762 | 0.94227 | -0.37487 |
| C | -2.38944 | 0.64904 | -0.11343 |
| C | -3.38986 | 1.60958 | -0.19368 |
| C | -3.05818 | 2.91355 | -0.54936 |
| H | -1.46607 | 4.24474 | -1.10728 |
| H | 0.27796 | 2.52175 | -0.96924 |
| H | -4.41887 | 1.34701 | 0.01688 |
| H | -3.83530 | 3.66566 | -0.61261 |
| I | -2.98859 | -1.33448 | 0.41185 |
| C | 0.02394 | -0.12163 | -0.28393 |
| H | -0.08108 | -0.65083 | 0.67493 |
| H | -0.18166 | -0.86267 | -1.06371 |
| N | 1.35143 | 0.42203 | -0.44956 |
| H | 1.55653 | 1.31405 | 0.00029 |
| C | 2.46702 | -0.40533 | -0.43267 |
| C | 2.40860 | -1.71112 | -0.94711 |
| C | 3.69740 | 0.07189 | 0.09438 |
| C | 3.54448 | -2.51021 | -1.00943 |
| H | 1.47090 | -2.10121 | -1.32304 |
| C | 4.82180 | -0.74816 | -0.00737 |
| C | 4.76692 | -2.02791 | -0.55458 |
| H | 3.46825 | -3.50854 | -1.42596 |
| H | 5.76719 | -0.36705 | 0.36287 |
| H | 5.66131 | -2.63620 | -0.61686 |
| C | 3.78173 | 1.42292 | 0.78252 |
| C | 4.60421 | 1.53123 | 1.87344 |
| H | 4.69069 | 2.48343 | 2.38556 |
| H | 5.16269 | 0.68858 | 2.25697 |
| O | 3.04644 | 2.37270 | 0.30152 |

**Prod (After SET): S6** in DMSO
31
-720.8779936

| | | | |
|---|---|---|---|
| C | -0.29112 | 4.12372 | -0.61728 |
| C | 0.31451 | 2.87992 | -0.77439 |
| C | -0.38679 | 1.69917 | -0.48625 |
| C | -1.68333 | 1.86308 | -0.05377 |
| C | -2.33425 | 3.06337 | 0.11437 |
| C | -1.61009 | 4.22314 | -0.17488 |
| H | 0.26851 | 5.02313 | -0.84530 |
| H | 1.34207 | 2.82051 | -1.12369 |
| H | -3.36100 | 3.11473 | 0.45925 |
| H | -2.07462 | 5.19552 | -0.05557 |
| I | -3.85375 | -1.38368 | 0.27772 |
| C | 0.24523 | 0.33809 | -0.65952 |
| H | -0.44703 | -0.41948 | -0.28130 |
| H | 0.38419 | 0.14130 | -1.73451 |
| N | 1.51346 | 0.27503 | 0.04836 |
| H | 2.02962 | 1.15368 | 0.11044 |
| C | 2.39091 | -0.77057 | -0.20320 |
| C | 1.95480 | -1.97628 | -0.77269 |
| C | 3.75368 | -0.63279 | 0.17082 |
| C | 2.84155 | -3.03180 | -0.97337 |
| H | 0.91548 | -2.09605 | -1.05332 |
| C | 4.61453 | -1.70319 | -0.05398 |
| C | 4.17793 | -2.90354 | -0.61767 |
| H | 2.47836 | -3.95268 | -1.41638 |
| H | 5.65947 | -1.58456 | 0.21187 |
| H | 4.87559 | -3.71593 | -0.78227 |
| C | 4.25431 | 0.66634 | 0.77392 |
| C | 5.13118 | 0.58570 | 1.82225 |
| H | 5.52006 | 1.49193 | 2.27420 |
| H | 5.45251 | -0.36795 | 2.21937 |
| O | 3.79664 | 1.75748 | 0.24915 |



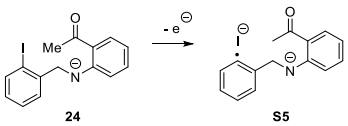
23 S6

**SM (Before SET): 23** in Benzene
31
-720.7166835

| | | | |
|---|---|---|---|
| C | 1.95348 | 3.49162 | 0.32429 |
| C | 0.84685 | 2.68145 | 0.09345 |
| C | 0.96490 | 1.29622 | -0.05250 |
| C | 2.25147 | 0.76030 | 0.06157 |
| C | 3.36928 | 1.55177 | 0.29358 |
| C | 3.22016 | 2.92943 | 0.42086 |
| H | 1.82198 | 4.56218 | 0.43195 |
| H | -0.14350 | 3.11596 | 0.03528 |
| H | 4.34895 | 1.09873 | 0.37888 |
| H | 4.09062 | 3.54936 | 0.60037 |
| I | 2.55873 | -1.34935 | -0.08140 |
| C | -0.23534 | 0.40943 | -0.30932 |
| H | -0.01426 | -0.28845 | -1.12271 |
| H | -0.39570 | -0.21943 | 0.57205 |
| N | -1.43803 | 1.17381 | -0.55074 |
| C | -2.74099 | 0.72080 | -0.27870 |
| C | -3.75412 | 1.68935 | -0.37674 |
| C | -3.08357 | -0.58863 | 0.11585 |
| C | -5.07693 | 1.39464 | -0.08291 |
| H | -3.47482 | 2.69722 | -0.66998 |
| C | -4.41787 | -0.84662 | 0.44621 |
| C | -5.41660 | 0.11700 | 0.35311 |
| H | -5.83315 | 2.16641 | -0.17796 |
| H | -4.66773 | -1.85817 | 0.74845 |
| H | -6.44308 | -0.12992 | 0.59916 |
| C | -2.11843 | -1.76731 | 0.04919 |
| C | -1.89246 | -2.45649 | 1.21635 |
| H | -1.24235 | -3.32494 | 1.21665 |
| H | -2.36416 | -2.15346 | 2.14264 |
| O | -1.63191 | -1.99588 | -1.10655 |
| H | -1.39316 | 1.75253 | -1.37867 |

**Prod (After SET): S6** in Benzene
31
-720.7688898

| | | | |
|---|---|---|---|
| C | 0.22378 | -0.62542 | 1.56039 |
| C | -0.93782 | -0.96737 | 0.86825 |
| C | -0.92013 | -1.11163 | -0.52647 |
| C | 0.29861 | -0.88846 | -1.13192 |
| C | 1.47568 | -0.55705 | -0.50636 |
| C | 1.42608 | -0.42157 | 0.88610 |
| H | 0.19064 | -0.52254 | 2.63925 |
| H | -1.87466 | -1.13961 | 1.39288 |
| H | 2.41227 | -0.40547 | -1.03320 |
| H | 2.33569 | -0.16509 | 1.41939 |
| I | 5.61979 | 0.21417 | 0.03942 |
| C | -2.17727 | -1.42426 | -1.31363 |
| H | -1.91548 | -2.00323 | -2.20158 |
| H | -2.86901 | -2.01933 | -0.72136 |
| N | -2.86556 | -0.21610 | -1.77958 |
| C | -3.46755 | 0.65558 | -0.85649 |
| C | -3.21249 | 2.02863 | -0.99772 |
| C | -4.33631 | 0.22473 | 0.17291 |
| C | -3.79911 | 2.97425 | -0.16748 |
| H | -2.52609 | 2.35105 | -1.77561 |
| C | -4.89400 | 1.19756 | 1.00673 |
| C | -4.64509 | 2.55900 | 0.85437 |
| H | -3.57910 | 4.02631 | -0.31291 |
| H | -5.56474 | 0.85644 | 1.78785 |
| H | -5.10736 | 3.27960 | 1.51947 |
| C | -4.76805 | -1.22544 | 0.36450 |
| C | -4.60962 | -1.74209 | 1.63093 |
| H | -4.90737 | -2.76420 | 1.83934 |
| H | -4.19063 | -1.14704 | 2.43272 |
| O | -5.23534 | -1.81857 | -0.66104 |
| H | -2.25173 | 0.30477 | -2.39479 |




**SM (Before SET): 24** in DMSO

31

-720.7637628

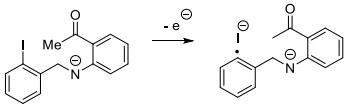
| | | | |
|---|---|---|---|
| C | -2.20085 | 3.46156 | -0.07705 |
| C | -1.04200 | 2.72823 | 0.15431 |
| C | -1.04319 | 1.33020 | 0.16128 |
| C | -2.26927 | 0.70695 | -0.08198 |
| C | -3.44070 | 1.41662 | -0.31935 |
| C | -3.40477 | 2.80811 | -0.31529 |
| H | -2.16245 | 4.54474 | -0.07323 |
| H | -0.09563 | 3.22109 | 0.33673 |
| H | -4.37106 | 0.89531 | -0.50637 |
| H | -4.31436 | 3.36731 | -0.49935 |
| I | -2.41008 | -1.43248 | -0.10797 |
| C | 0.22554 | 0.53757 | 0.41749 |
| H | 0.03072 | -0.15127 | 1.25273 |
| H | 0.38086 | -0.13623 | -0.44661 |
| N | 1.36147 | 1.37618 | 0.64572 |
| C | 2.56248 | 0.92364 | 0.35296 |
| C | 3.64247 | 1.89392 | 0.33478 |
| C | 2.94688 | -0.42694 | -0.04956 |
| C | 4.83261 | 1.64901 | -0.28618 |
| H | 3.43313 | 2.86716 | 0.76734 |
| C | 4.16815 | -0.60837 | -0.75104 |
| C | 5.09689 | 0.39343 | -0.89877 |
| H | 5.58578 | 2.43047 | -0.32256 |
| H | 4.40734 | -1.59716 | -1.12881 |
| H | 6.03183 | 0.21465 | -1.41465 |
| C | 2.27380 | -1.61825 | 0.44272 |
| C | 2.47154 | -2.93961 | -0.28996 |
| H | 1.63342 | -3.59039 | -0.04261 |
| H | 2.53681 | -2.81815 | -1.37121 |
| O | 1.60020 | -1.63374 | 1.47875 |
| H | 3.38859 | -3.42573 | 0.05498 |

**Prod (After SET): S5** in DMSO

31

-720.8694189

| | | | |
|---|---|---|---|
| C | -0.12726 | 4.73811 | -0.29030 |
| C | 0.59354 | 3.56886 | -0.03737 |
| C | -0.06068 | 2.35267 | 0.19168 |
| C | -1.43972 | 2.41520 | 0.14479 |
| C | -2.20452 | 3.52685 | -0.10270 |
| C | -1.51850 | 4.72849 | -0.32542 |
| H | 0.40607 | 5.66608 | -0.46306 |
| H | 1.67650 | 3.57633 | -0.01065 |
| H | -3.28796 | 3.48719 | -0.12616 |
| H | -2.07094 | 5.63989 | -0.52472 |
| I | -3.16960 | -1.52326 | -0.16550 |
| C | 0.66061 | 1.04467 | 0.46486 |
| H | 0.20811 | 0.58976 | 1.35745 |
| H | 0.40462 | 0.34224 | -0.35134 |
| N | 2.07679 | 1.22118 | 0.58362 |
| C | 2.88005 | 0.21915 | 0.29758 |
| C | 4.29244 | 0.52887 | 0.15888 |
| C | 2.52811 | -1.17000 | 0.01044 |
| C | 5.16694 | -0.31217 | -0.46550 |
| H | 4.61529 | 1.50592 | 0.50409 |
| C | 3.45646 | -1.97711 | -0.69851 |
| C | 4.74396 | -1.57602 | -0.96158 |
| H | 6.20124 | -0.00669 | -0.59257 |
| H | 3.15763 | -2.97981 | -0.98607 |
| H | 5.43604 | -2.22797 | -1.47949 |
| C | 1.39745 | -1.84287 | 0.63018 |
| C | 0.87579 | -3.13832 | 0.02083 |
| H | -0.17265 | -3.23881 | 0.30071 |
| H | 0.96538 | -3.16478 | -1.06511 |
| O | 0.87752 | -1.45648 | 1.68292 |
| H | 1.42365 | -3.99111 | 0.43250 |




**SM (Before SET): 24** in Benzene

31

-720.7285731

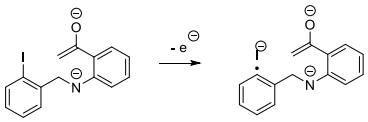
| | | | |
|---|---|---|---|
| C | -2.18980 | 3.45870 | -0.05112 |
| C | -1.03485 | 2.71818 | 0.17078 |
| C | -1.04312 | 1.31980 | 0.16445 |
| C | -2.27245 | 0.70673 | -0.08112 |
| C | -3.44121 | 1.42377 | -0.30962 |
| C | -3.39835 | 2.81440 | -0.29330 |
| H | -2.14542 | 4.54188 | -0.03705 |
| H | -0.08056 | 3.19532 | 0.35661 |
| H | -4.37315 | 0.90612 | -0.49875 |
| H | -4.30555 | 3.38028 | -0.47054 |
| I | -2.42166 | -1.43147 | -0.11951 |
| C | 0.22662 | 0.52742 | 0.41330 |
| H | 0.04317 | -0.15339 | 1.25819 |
| H | 0.37258 | -0.15199 | -0.44832 |
| N | 1.35739 | 1.37496 | 0.62057 |
| C | 2.55791 | 0.92505 | 0.33874 |
| C | 3.62996 | 1.90546 | 0.30819 |
| C | 2.95605 | -0.42924 | -0.04229 |
| C | 4.82307 | 1.66330 | -0.30466 |
| H | 3.40487 | 2.88034 | 0.72814 |
| C | 4.18203 | -0.60738 | -0.73388 |
| C | 5.10250 | 0.39995 | -0.89545 |
| H | 5.56891 | 2.45178 | -0.35078 |
| H | 4.43348 | -1.59961 | -1.09484 |
| H | 6.04137 | 0.22084 | -1.40455 |
| C | 2.28816 | -1.61958 | 0.46027 |
| C | 2.51571 | -2.95171 | -0.25343 |
| H | 1.68206 | -3.60654 | -0.00168 |
| H | 2.58820 | -2.84432 | -1.33619 |
| O | 1.59583 | -1.63596 | 1.47951 |
| H | 3.43603 | -3.41900 | 0.10860 |

**Prod (After SET): S5** in Benzene

31

-720.7602330

| | | | |
|---|---|---|---|
| C | -0.01608 | 4.58619 | 0.09895 |
| C | 0.77667 | 3.45780 | 0.30054 |
| C | 0.22023 | 2.17253 | 0.27831 |
| C | -1.13855 | 2.12368 | 0.03455 |
| C | -1.97289 | 3.19610 | -0.18130 |
| C | -1.38205 | 4.46482 | -0.13940 |
| H | 0.43818 | 5.57096 | 0.12420 |
| H | 1.84390 | 3.54053 | 0.46829 |
| H | -3.03180 | 3.06234 | -0.37175 |
| H | -1.98982 | 5.34934 | -0.30106 |
| I | -4.08618 | -1.28295 | -0.25067 |
| C | 1.04633 | 0.92658 | 0.54448 |
| H | 0.81618 | 0.58873 | 1.56452 |
| H | 0.67294 | 0.11511 | -0.10418 |
| N | 2.44737 | 1.17976 | 0.35099 |
| C | 3.28475 | 0.19962 | 0.06265 |
| C | 4.60367 | 0.59925 | -0.40900 |
| C | 3.05956 | -1.25257 | 0.06143 |
| C | 5.42367 | -0.24806 | -1.09274 |
| H | 4.86884 | 1.64267 | -0.27111 |
| C | 3.90981 | -2.07001 | -0.72305 |
| C | 5.05781 | -1.60390 | -1.31921 |
| H | 6.36941 | 0.12243 | -1.47929 |
| H | 3.67669 | -3.12735 | -0.80592 |
| H | 5.69738 | -2.26436 | -1.89189 |
| C | 2.17480 | -1.92161 | 1.00288 |
| C | 1.73663 | -3.35500 | 0.70955 |
| H | 0.86960 | -3.57069 | 1.33208 |
| H | 1.48100 | -3.50458 | -0.34033 |
| O | 1.81047 | -1.42289 | 2.07009 |
| H | 2.53366 | -4.05661 | 0.97234 |



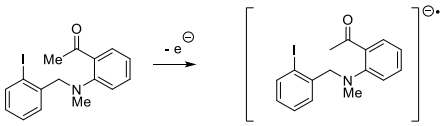
25 S7

**SM (Before SET): 25** in DMSO
30
-720.2417849

| | | | |
|---|---|---|---|
| C | -2.13089 | 3.48667 | -0.12209 |
| C | -0.97347 | 2.73231 | 0.04084 |
| C | -0.99777 | 1.33398 | 0.07945 |
| C | -2.25369 | 0.73645 | -0.05454 |
| C | -3.42555 | 1.46515 | -0.22085 |
| C | -3.36283 | 2.85581 | -0.25400 |
| H | -2.07005 | 4.56888 | -0.14653 |
| H | -0.00328 | 3.20129 | 0.14433 |
| H | -4.37746 | 0.95970 | -0.32513 |
| H | -4.27271 | 3.42997 | -0.38273 |
| I | -2.44726 | -1.40102 | -0.02193 |
| C | 0.27881 | 0.53079 | 0.25413 |
| H | 0.11289 | -0.16544 | 1.09151 |
| H | 0.36219 | -0.13072 | -0.62542 |
| N | 1.43073 | 1.36730 | 0.42583 |
| C | 2.64890 | 0.85584 | 0.21220 |
| C | 3.74308 | 1.79505 | 0.21477 |
| C | 3.03607 | -0.51994 | -0.05388 |
| C | 5.03922 | 1.46447 | -0.12249 |
| H | 3.49560 | 2.82383 | 0.46250 |
| C | 4.35689 | -0.80503 | -0.41034 |
| C | 5.37358 | 0.14917 | -0.47220 |
| H | 5.80204 | 2.23874 | -0.11717 |
| H | 4.59688 | -1.84559 | -0.61364 |
| H | 6.38640 | -0.12705 | -0.74045 |
| C | 2.14051 | -1.72034 | 0.19779 |
| C | 1.91602 | -2.60199 | -0.83717 |
| H | 1.34690 | -3.51182 | -0.66687 |
| H | 2.29324 | -2.40793 | -1.83337 |
| O | 1.71046 | -1.86263 | 1.40308 |

**Prod (After SET): S7** in DMSO
30
-720.3443286

| | | | |
|---|---|---|---|
| C | -0.57977 | 4.53469 | -0.00855 |
| C | 0.31687 | 3.46577 | 0.07255 |
| C | -0.13711 | 2.14321 | 0.15123 |
| C | -1.51198 | 2.00012 | 0.14122 |
| C | -2.44244 | 3.00519 | 0.05829 |
| C | -1.95449 | 4.31761 | -0.01640 |
| H | -0.19722 | 5.54765 | -0.06890 |
| H | 1.38770 | 3.62885 | 0.07119 |
| H | -3.50786 | 2.80136 | 0.04814 |
| H | -2.64486 | 5.15122 | -0.08282 |
| I | -3.41021 | -1.54257 | -0.24121 |
| C | 0.78877 | 0.94584 | 0.25871 |
| H | 0.56355 | 0.44944 | 1.21651 |
| H | 0.46588 | 0.21852 | -0.50715 |
| N | 2.16839 | 1.31608 | 0.10750 |
| C | 3.08345 | 0.35217 | -0.04701 |
| C | 4.39701 | 0.77627 | -0.46230 |
| C | 2.93760 | -1.08529 | 0.11904 |
| C | 5.41167 | -0.09413 | -0.80333 |
| H | 4.55343 | 1.84831 | -0.54447 |
| C | 3.98533 | -1.92995 | -0.25723 |
| C | 5.21760 | -1.48072 | -0.73527 |
| H | 6.36654 | 0.30701 | -1.13324 |
| H | 3.82722 | -2.99753 | -0.12737 |
| H | 6.00296 | -2.17726 | -1.00337 |
| C | 1.78899 | -1.73937 | 0.86806 |
| C | 1.06583 | -2.72735 | 0.23909 |
| H | 0.29276 | -3.26830 | 0.77778 |
| H | 1.24134 | -2.97837 | -0.79969 |
| O | 1.62589 | -1.36143 | 2.08955 |



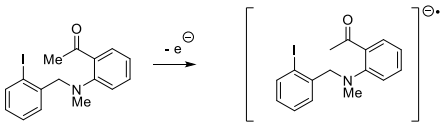

18 S8

**SM (Before SET): 18** in DMSO
35
-760.5580475

| | | | |
|---|---|---|---|
| C | 1.17159 | 2.91478 | -1.35050 |
| C | 0.39692 | 1.79919 | -1.05438 |
| C | 0.96541 | 0.63198 | -0.53866 |
| C | 2.34386 | 0.63423 | -0.32314 |
| C | 3.13636 | 1.73911 | -0.61173 |
| C | 2.54405 | 2.88513 | -1.13258 |
| H | 0.70187 | 3.80519 | -1.75025 |
| H | -0.67450 | 1.83050 | -1.21893 |
| H | 4.20336 | 1.70937 | -0.43265 |
| H | 3.15798 | 3.74771 | -1.36207 |
| I | 3.31460 | -1.08076 | 0.50404 |
| C | 0.10841 | -0.58845 | -0.22601 |
| H | 0.50454 | -1.44412 | -0.78291 |
| H | 0.20766 | -0.84492 | 0.83225 |
| N | -1.29351 | -0.46107 | -0.55722 |
| C | -2.17786 | 0.11159 | 0.34451 |
| C | -1.70761 | 0.90016 | 1.41330 |
| C | -3.57716 | -0.05282 | 0.21581 |
| C | -2.58790 | 1.53872 | 2.27296 |
| H | -0.64412 | 1.04926 | 1.54950 |
| C | -4.44414 | 0.64770 | 1.06088 |
| C | -3.96658 | 1.44078 | 2.09212 |
| H | -2.18769 | 2.14153 | 3.08020 |
| H | -5.51064 | 0.51279 | 0.91895 |
| H | -4.65090 | 1.95635 | 2.75365 |
| C | -4.22614 | -1.05657 | -0.68456 |
| C | -3.69737 | -2.47242 | -0.67154 |
| H | -3.77441 | -2.90892 | -1.66778 |
| H | -2.67948 | -2.54373 | -0.29411 |
| O | -5.23879 | -0.78360 | -1.29844 |
| C | -1.60837 | -0.61690 | -1.97276 |
| H | -1.71214 | -1.66758 | -2.25759 |
| H | -2.52963 | -0.08735 | -2.21793 |
| H | -0.80659 | -0.17886 | -2.57418 |
| H | -4.35511 | -3.03815 | -0.00457 |

**Prod (After SET): 56** in DMSO
35
-760.6360878

| | | | |
|---|---|---|---|
| C | -1.28159 | 2.92099 | 1.34846 |
| C | -0.47075 | 1.84238 | 1.01702 |
| C | -1.00016 | 0.65891 | 0.49258 |
| C | -2.38104 | 0.61684 | 0.30140 |
| C | -3.21250 | 1.68403 | 0.62430 |
| C | -2.65691 | 2.84220 | 1.15687 |
| H | -0.83876 | 3.82322 | 1.75305 |
| H | 0.60273 | 1.91189 | 1.14984 |
| H | -4.28031 | 1.61524 | 0.46125 |
| H | -3.29946 | 3.67589 | 1.41326 |
| I | -3.30856 | -1.11024 | -0.55715 |
| C | -0.09955 | -0.52611 | 0.14646 |
| H | -0.53105 | -1.41513 | 0.62346 |
| H | -0.14663 | -0.70099 | -0.93346 |
| N | 1.28045 | -0.44230 | 0.54767 |
| C | 2.23469 | 0.18996 | -0.28266 |
| C | 1.82818 | 1.13168 | -1.22130 |
| C | 3.64485 | -0.14034 | -0.16981 |
| C | 2.74029 | 1.86313 | -2.00335 |
| H | 0.77153 | 1.35258 | -1.32292 |
| C | 4.54328 | 0.74744 | -0.85358 |
| C | 4.10843 | 1.69586 | -1.75970 |
| H | 2.37932 | 2.58421 | -2.72683 |
| H | 5.60317 | 0.58080 | -0.70649 |
| H | 4.83536 | 2.29727 | -2.29701 |
| C | 4.22621 | -1.27000 | 0.49627 |
| C | 3.43661 | -2.52164 | 0.83636 |
| H | 3.43290 | -2.70287 | 1.91769 |
| H | 2.40862 | -2.50622 | 0.47984 |
| O | 5.48414 | -1.33347 | 0.71672 |
| C | 1.49760 | -0.53977 | 1.98416 |
| H | 1.22014 | -1.53661 | 2.34180 |
| H | 2.54962 | -0.37562 | 2.20910 |
| H | 0.90599 | 0.19667 | 2.54148 |
| H | 3.95840 | -3.36711 | 0.37692 |



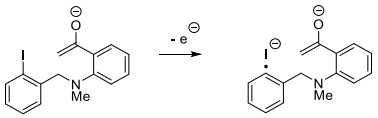

18 S8

**SM (Before SET): 18** in Benzene
35
-760.5528685

| | | | |
|---|---|---|---|
| C | 1.17064 | 2.91392 | -1.34787 |
| C | 0.39581 | 1.80080 | -1.04477 |
| C | 0.96569 | 0.63368 | -0.53082 |
| C | 2.34506 | 0.63355 | -0.32293 |
| C | 3.13734 | 1.73630 | -0.61900 |
| C | 2.54411 | 2.88176 | -1.13880 |
| H | 0.69997 | 3.80483 | -1.74537 |
| H | -0.67708 | 1.83368 | -1.19925 |
| H | 4.20513 | 1.70376 | -0.44559 |
| H | 3.15806 | 3.74280 | -1.37400 |
| I | 3.31647 | -1.07943 | 0.50486 |
| C | 0.10797 | -0.58486 | -0.21153 |
| H | 0.50997 | -1.44434 | -0.75892 |
| H | 0.20403 | -0.83227 | 0.84937 |
| N | -1.29224 | -0.46377 | -0.54826 |
| C | -2.18307 | 0.11612 | 0.34770 |
| C | -1.72013 | 0.91778 | 1.40785 |
| C | -3.57909 | -0.05876 | 0.21437 |
| C | -2.60789 | 1.55806 | 2.25910 |
| H | -0.65789 | 1.07681 | 1.54337 |
| C | -4.45357 | 0.64475 | 1.04718 |
| C | -3.98403 | 1.44955 | 2.07324 |
| H | -2.21503 | 2.17159 | 3.06177 |
| H | -5.51823 | 0.50633 | 0.89566 |
| H | -4.67402 | 1.96898 | 2.72573 |
| C | -4.21838 | -1.07102 | -0.68716 |
| C | -3.68598 | -2.48741 | -0.65231 |
| H | -3.77642 | -2.94187 | -1.63928 |
| H | -2.66346 | -2.54903 | -0.28505 |
| O | -5.21979 | -0.80533 | -1.31608 |
| C | -1.60157 | -0.61381 | -1.96492 |
| H | -1.70887 | -1.66372 | -2.25367 |
| H | -2.52182 | -0.08306 | -2.21159 |
| H | -0.79677 | -0.17651 | -2.56355 |
| H | -4.33416 | -3.04155 | 0.03328 |

**Prod (After SET): 56** in Benzene
35
-760.5987172

| | | | |
|---|---|---|---|
| C | -1.27974 | 2.92331 | 1.33531 |
| C | -0.46954 | 1.84840 | 0.99360 |
| C | -1.00141 | 0.66291 | 0.47487 |
| C | -2.38346 | 0.61916 | 0.30102 |
| C | -3.21568 | 1.68247 | 0.63392 |
| C | -2.65734 | 2.84122 | 1.16087 |
| H | -0.83349 | 3.82712 | 1.73281 |
| H | 0.60618 | 1.91911 | 1.10698 |
| H | -4.28473 | 1.60863 | 0.48135 |
| H | -3.29889 | 3.67354 | 1.42498 |
| I | -3.31652 | -1.10828 | -0.55460 |
| C | -0.09505 | -0.51724 | 0.12097 |
| H | -0.53540 | -1.41169 | 0.58148 |
| H | -0.13149 | -0.67393 | -0.96243 |
| N | 1.27689 | -0.43700 | 0.53460 |
| C | 2.24630 | 0.19544 | -0.28947 |
| C | 1.85441 | 1.15446 | -1.21444 |
| C | 3.64908 | -0.15210 | -0.16559 |
| C | 2.77914 | 1.88368 | -1.98363 |
| H | 0.80025 | 1.38804 | -1.31995 |
| C | 4.56255 | 0.73286 | -0.83299 |
| C | 4.14505 | 1.69403 | -1.72959 |
| H | 2.43246 | 2.61605 | -2.70267 |
| H | 5.61783 | 0.55002 | -0.67239 |
| H | 4.88392 | 2.29181 | -2.25510 |
| C | 4.21975 | -1.29083 | 0.49928 |
| C | 3.41095 | -2.53918 | 0.82168 |
| H | 3.39799 | -2.72612 | 1.90222 |
| H | 2.38714 | -2.51298 | 0.45224 |
| O | 5.46387 | -1.36608 | 0.73638 |
| C | 1.48624 | -0.53031 | 1.97019 |
| H | 1.18120 | -1.51848 | 2.33234 |
| H | 2.54354 | -0.39708 | 2.19225 |
| H | 0.91705 | 0.22543 | 2.52787 |
| H | 3.93566 | -3.38245 | 0.36247 |




22 S9

**SM (Before SET): 22** in DMSO
34
-760.0540185

| | | | |
|---|---|---|---|
| C | 1.10317 | 2.95839 | -1.21223 |
| C | 0.34944 | 1.81571 | -0.97215 |
| C | 0.93793 | 0.63535 | -0.51100 |
| C | 2.31536 | 0.65403 | -0.29513 |
| C | 3.08908 | 1.78556 | -0.52685 |
| C | 2.47607 | 2.94464 | -0.99176 |
| H | 0.61775 | 3.85860 | -1.56958 |
| H | -0.72282 | 1.82904 | -1.13443 |
| H | 4.15660 | 1.76629 | -0.34843 |
| H | 3.07381 | 3.82903 | -1.17678 |
| I | 3.32002 | -1.08871 | 0.43335 |
| C | 0.09410 | -0.61069 | -0.25803 |
| H | 0.50511 | -1.42861 | -0.86055 |
| H | 0.20993 | -0.91637 | 0.78614 |
| N | -1.30606 | -0.48919 | -0.57416 |
| C | -2.20050 | 0.03460 | 0.35991 |
| C | -1.71345 | 0.76590 | 1.46304 |
| C | -3.59808 | -0.15726 | 0.24979 |
| C | -2.57206 | 1.31749 | 2.40536 |
| H | -0.64908 | 0.93206 | 1.57414 |
| C | -4.43539 | 0.44762 | 1.18760 |
| C | -3.94905 | 1.17864 | 2.26694 |
| H | -2.15581 | 1.87252 | 3.23881 |
| H | -5.50547 | 0.29998 | 1.07479 |
| H | -4.62828 | 1.61458 | 2.98990 |
| C | -4.27713 | -1.02947 | -0.79815 |
| C | -4.09119 | -2.38033 | -0.67816 |
| H | -4.55271 | -3.06408 | -1.38395 |
| H | -3.44126 | -2.78461 | 0.08817 |
| O | -4.99815 | -0.41656 | -1.66733 |
| C | -1.62969 | -0.60499 | -1.98951 |
| H | -1.73882 | -1.64958 | -2.29449 |
| H | -2.56231 | -0.08776 | -2.21003 |
| H | -0.83169 | -0.14374 | -2.58152 |

**Prod (After SET): S9** in DMSO
34
-760.1608524

| | | | |
|---|---|---|---|
| C | -0.08793 | 3.88895 | -0.46274 |
| C | -0.51017 | 2.56010 | -0.50459 |
| C | 0.41306 | 1.51192 | -0.41907 |
| C | 1.73347 | 1.88821 | -0.29312 |
| C | 2.20806 | 3.17555 | -0.24215 |
| C | 1.26180 | 4.20397 | -0.33187 |
| H | -0.82136 | 4.68372 | -0.53236 |
| H | -1.56625 | 2.32683 | -0.60049 |
| H | 3.26496 | 3.39481 | -0.13841 |
| H | 1.58291 | 5.23899 | -0.29935 |
| I | 4.06952 | -1.34618 | 0.20229 |
| C | 0.00211 | 0.04343 | -0.46170 |
| H | 0.57196 | -0.44550 | -1.25831 |
| H | 0.30973 | -0.44240 | 0.46822 |
| N | -1.40012 | -0.20127 | -0.70118 |
| C | -2.31284 | -0.19776 | 0.35285 |
| C | -1.95134 | 0.36198 | 1.59611 |
| C | -3.60717 | -0.75748 | 0.22363 |
| C | -2.84376 | 0.40830 | 2.65914 |
| H | -0.96769 | 0.79613 | 1.72584 |
| C | -4.49556 | -0.64979 | 1.29393 |
| C | -4.13807 | -0.08057 | 2.51199 |
| H | -2.52575 | 0.84918 | 3.59757 |
| H | -5.48959 | -1.06749 | 1.16352 |
| H | -4.84656 | -0.03427 | 3.33042 |
| C | -4.10417 | -1.54433 | -0.98245 |
| C | -3.47595 | -2.73512 | -1.23176 |
| H | -3.78464 | -3.35557 | -2.06743 |
| H | -2.62370 | -3.04630 | -0.64004 |
| O | -5.10289 | -1.04414 | -1.61810 |
| C | -1.82033 | -0.04486 | -2.08653 |
| H | -1.67056 | -0.96348 | -2.66083 |
| H | -2.87676 | 0.21640 | -2.13601 |
| H | -1.24481 | 0.76353 | -2.55067 |

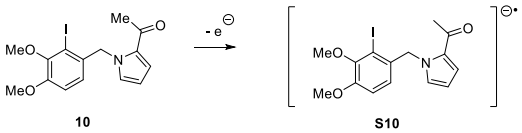
22 S9

**SM (Before SET): 22** in Benzene
34
-760.0128981

| | | | |
|---|---|---|---|
| C | 1.09738 | 2.96578 | -1.17597 |
| C | 0.34622 | 1.82122 | -0.94106 |
| C | 0.93858 | 0.63743 | -0.49306 |
| C | 2.31605 | 0.65793 | -0.28593 |
| C | 3.08877 | 1.79103 | -0.51229 |
| C | 2.47170 | 2.95270 | -0.96380 |
| H | 0.60754 | 3.86807 | -1.52217 |
| H | -0.72761 | 1.82968 | -1.09364 |
| H | 4.15725 | 1.76895 | -0.33986 |
| H | 3.06700 | 3.83978 | -1.14501 |
| I | 3.32796 | -1.09211 | 0.41862 |
| C | 0.08851 | -0.60794 | -0.24737 |
| H | 0.50220 | -1.42409 | -0.85135 |
| H | 0.20165 | -0.91531 | 0.79705 |
| N | -1.30407 | -0.47543 | -0.57001 |
| C | -2.20638 | 0.03111 | 0.36981 |
| C | -1.72297 | 0.74641 | 1.48373 |
| C | -3.60158 | -0.16744 | 0.25163 |
| C | -2.58537 | 1.26945 | 2.44004 |
| H | -0.65982 | 0.92174 | 1.59618 |
| C | -4.44071 | 0.40528 | 1.20492 |
| C | -3.95935 | 1.11579 | 2.30127 |
| H | -2.17301 | 1.81163 | 3.28422 |
| H | -5.50859 | 0.25093 | 1.08361 |
| H | -4.64240 | 1.52780 | 3.03511 |
| C | -4.27742 | -0.98861 | -0.84479 |
| C | -4.21461 | -2.35012 | -0.69650 |
| H | -4.68783 | -3.00029 | -1.42517 |
| H | -3.69416 | -2.79474 | 0.14299 |
| O | -4.85424 | -0.31951 | -1.76686 |
| C | -1.62784 | -0.61240 | -1.98389 |
| H | -1.74306 | -1.66224 | -2.26946 |
| H | -2.55995 | -0.09832 | -2.21427 |
| H | -0.82479 | -0.16359 | -2.58072 |

**Prod (After SET): S9** in Benzene
34
-760.0619544

| | | | |
|---|---|---|---|
| C | -0.86869 | 0.38184 | 1.54492 |
| C | 0.32970 | 0.07187 | 0.90057 |
| C | 0.32681 | -0.45906 | -0.39382 |
| C | -0.91809 | -0.64967 | -0.95517 |
| C | -2.12851 | -0.36316 | -0.37665 |
| C | -2.09366 | 0.17177 | 0.91697 |
| H | -0.84187 | 0.79127 | 2.54825 |
| H | 1.28364 | 0.23667 | 1.39379 |
| H | -3.08269 | -0.53119 | -0.86614 |
| H | -3.03037 | 0.41252 | 1.40874 |
| I | -6.24127 | 0.04238 | -0.05047 |
| C | 1.60859 | -0.79982 | -1.14733 |
| H | 1.48547 | -1.79534 | -1.59014 |
| H | 1.72572 | -0.10370 | -1.98266 |
| N | 2.81324 | -0.80106 | -0.35876 |
| C | 3.62290 | 0.33097 | -0.27381 |
| C | 3.06359 | 1.60435 | -0.50383 |
| C | 5.00123 | 0.24471 | 0.03115 |
| C | 3.82937 | 2.75937 | -0.40825 |
| H | 2.00624 | 1.69193 | -0.72653 |
| C | 5.72994 | 1.42472 | 0.16718 |
| C | 5.17210 | 2.68091 | -0.05339 |
| H | 3.36234 | 3.72167 | -0.58969 |
| H | 6.78144 | 1.33329 | 0.42209 |
| H | 5.77515 | 3.57721 | 0.03707 |
| C | 5.78312 | -1.05826 | 0.18873 |
| C | 6.00580 | -1.76452 | -0.96666 |
| H | 6.56924 | -2.69176 | -0.93897 |
| H | 5.60057 | -1.42374 | -1.91181 |
| O | 6.18349 | -1.33379 | 1.36947 |
| C | 3.00733 | -1.97024 | 0.48072 |
| H | 3.36365 | -2.82830 | -0.09903 |
| H | 3.74304 | -1.76336 | 1.25663 |
| H | 2.05582 | -2.23022 | 0.96071 |




**SM (Before SET): 10** in DMSO

36

-872.8836869

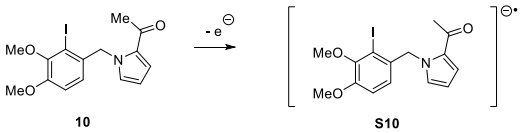
| | | | |
|---|---|---|---|
| C | -1.96544 | 0.81152 | -0.17338 |
| C | -1.00435 | -0.17946 | -0.33007 |
| C | 0.33089 | 0.12059 | -0.62009 |
| C | 0.66733 | 1.46174 | -0.75635 |
| C | -0.27305 | 2.47850 | -0.60402 |
| C | -1.59346 | 2.16234 | -0.30995 |
| H | 0.03828 | 3.50754 | -0.71864 |
| C | 1.36737 | -0.97159 | -0.79597 |
| H | 1.27409 | -1.70711 | -0.00059 |
| H | 1.21870 | -1.48297 | -1.75027 |
| N | 2.72664 | -0.45207 | -0.79760 |
| C | 3.44646 | -0.22705 | -1.92574 |
| C | 3.43660 | 0.02575 | 0.28984 |
| C | 4.64092 | 0.38430 | -1.58873 |
| H | 3.05544 | -0.52207 | -2.88778 |
| C | 4.63367 | 0.54343 | -0.19054 |
| H | 5.41378 | 0.97917 | 0.41478 |
| H | 5.42041 | 0.67067 | -2.27614 |
| C | 2.95885 | -0.02559 | 1.67194 |
| C | 3.87716 | 0.55722 | 2.71998 |
| H | 4.03580 | 1.62139 | 2.53234 |
| H | 3.42584 | 0.42273 | 3.70073 |
| O | 1.87773 | -0.50606 | 1.97463 |
| H | 1.69264 | 1.73165 | -0.98453 |
| O | -3.26846 | 0.50309 | 0.07751 |
| O | -2.59016 | 3.06123 | -0.14013 |
| C | -2.25604 | 4.43827 | -0.25500 |
| H | -3.17922 | 4.98437 | -0.07952 |
| H | -1.51242 | 4.72195 | 0.49416 |
| H | -1.87907 | 4.66522 | -1.25545 |
| C | -3.63262 | 0.64740 | 1.45495 |
| H | -3.03436 | -0.02908 | 2.07147 |
| H | -3.48919 | 1.67966 | 1.77950 |
| H | -4.68415 | 0.37763 | 1.52667 |
| I | -1.65459 | -2.19532 | -0.12249 |
| H | 4.85148 | 0.06562 | 2.69135 |

**Prod (After SET): S10** in DMSO

36

-872.9563131

| | | | |
|---|---|---|---|
| C | -1.95406 | 0.87453 | -0.12500 |
| C | -1.02696 | -0.14850 | -0.28420 |
| C | 0.32967 | 0.09728 | -0.51639 |
| C | 0.72813 | 1.42881 | -0.57729 |
| C | -0.17443 | 2.47871 | -0.41780 |
| C | -1.51931 | 2.21108 | -0.19171 |
| H | 0.18427 | 3.49743 | -0.47383 |
| C | 1.33257 | -1.03389 | -0.68542 |
| H | 1.27313 | -1.68969 | 0.18064 |
| H | 1.08008 | -1.61098 | -1.58079 |
| N | 2.69648 | -0.57467 | -0.82232 |
| C | 3.19566 | -0.14150 | -2.04615 |
| C | 3.47685 | -0.03921 | 0.21881 |
| C | 4.31444 | 0.62370 | -1.81418 |
| H | 2.70733 | -0.43077 | -2.96425 |
| C | 4.50727 | 0.70451 | -0.41376 |
| H | 5.32220 | 1.19944 | 0.09157 |
| H | 4.94194 | 1.06173 | -2.57701 |
| C | 3.23826 | -0.28433 | 1.59693 |
| C | 4.13014 | 0.41778 | 2.59869 |
| H | 4.57589 | 1.33454 | 2.20687 |
| H | 3.54231 | 0.67184 | 3.48558 |
| O | 2.36114 | -1.12313 | 2.04097 |
| H | 1.77479 | 1.65306 | -0.75118 |
| O | -3.27987 | 0.61410 | 0.06435 |
| O | -2.48420 | 3.14854 | -0.02552 |
| C | -2.08386 | 4.51101 | -0.06516 |
| H | -2.98760 | 5.09263 | 0.09827 |
| H | -1.35949 | 4.72788 | 0.72423 |
| H | -1.65553 | 4.76385 | -1.03858 |
| C | -3.68539 | 0.71142 | 1.43328 |
| H | -3.13363 | -0.01328 | 2.03849 |
| H | -3.51597 | 1.72229 | 1.80917 |
| H | -4.74801 | 0.47844 | 1.45977 |
| I | -1.76334 | -2.14690 | -0.16581 |
| H | 4.94927 | -0.23445 | 2.93288 |



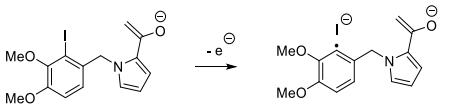

10 S10

**SM (Before SET): 10** in Benzene
36
-872.8766886

| | | | |
|---|---|---|---|
| C | -1.97292 | 0.81331 | -0.17019 |
| C | -1.01345 | -0.18100 | -0.30894 |
| C | 0.32712 | 0.11309 | -0.57992 |
| C | 0.67237 | 1.45094 | -0.71710 |
| C | -0.26657 | 2.47152 | -0.58061 |
| C | -1.59146 | 2.16168 | -0.30368 |
| H | 0.05029 | 3.49907 | -0.69334 |
| C | 1.35773 | -0.98771 | -0.73094 |
| H | 1.27974 | -1.68663 | 0.09886 |
| H | 1.18542 | -1.54055 | -1.65799 |
| N | 2.71858 | -0.47425 | -0.78687 |
| C | 3.40334 | -0.27792 | -1.94234 |
| C | 3.46552 | 0.02108 | 0.26576 |
| C | 4.61093 | 0.33207 | -1.65726 |
| H | 2.98012 | -0.59108 | -2.88473 |
| C | 4.64932 | 0.51981 | -0.26261 |
| H | 5.45092 | 0.96310 | 0.30804 |
| H | 5.37031 | 0.59729 | -2.37481 |
| C | 3.02296 | 0.00583 | 1.66335 |
| C | 3.98161 | 0.59203 | 2.67507 |
| H | 4.15495 | 1.64925 | 2.46239 |
| H | 3.55103 | 0.48444 | 3.66832 |
| O | 1.94423 | -0.44538 | 2.00314 |
| H | 1.70223 | 1.71478 | -0.93136 |
| O | -3.27929 | 0.50959 | 0.05750 |
| O | -2.58672 | 3.06626 | -0.14654 |
| C | -2.25187 | 4.43645 | -0.28717 |
| H | -3.17660 | 4.98700 | -0.13324 |
| H | -1.51516 | 4.73909 | 0.46247 |
| H | -1.86460 | 4.64344 | -1.28876 |
| C | -3.67247 | 0.66506 | 1.42302 |
| H | -3.07928 | 0.00351 | 2.06081 |
| H | -3.55023 | 1.70307 | 1.73865 |
| H | -4.72185 | 0.38216 | 1.47477 |
| I | -1.67454 | -2.19187 | -0.10688 |
| H | 4.94485 | 0.07987 | 2.63161 |

**Prod (After SET): S10** in Benzene
36
-872.9164480

| | | | |
|---|---|---|---|
| C | -1.93883 | 0.89430 | -0.14198 |
| C | -1.02837 | -0.14634 | -0.28076 |
| C | 0.33373 | 0.06848 | -0.50136 |
| C | 0.75808 | 1.39113 | -0.58105 |
| C | -0.12685 | 2.45799 | -0.44273 |
| C | -1.47697 | 2.21870 | -0.21967 |
| H | 0.25337 | 3.46842 | -0.50706 |
| C | 1.32330 | -1.08089 | -0.62540 |
| H | 1.26605 | -1.68677 | 0.27811 |
| H | 1.05299 | -1.69825 | -1.48861 |
| N | 2.68731 | -0.64301 | -0.79768 |
| C | 3.17898 | -0.25843 | -2.04234 |
| C | 3.47775 | -0.07041 | 0.21705 |
| C | 4.30457 | 0.50794 | -1.84552 |
| H | 2.68593 | -0.58313 | -2.94574 |
| C | 4.50844 | 0.64248 | -0.45195 |
| H | 5.33087 | 1.14826 | 0.02955 |
| H | 4.93075 | 0.91012 | -2.62907 |
| C | 3.23167 | -0.25176 | 1.60295 |
| C | 4.14171 | 0.48209 | 2.56841 |
| H | 4.54468 | 1.40949 | 2.15262 |
| H | 3.57350 | 0.71958 | 3.47174 |
| O | 2.33613 | -1.03716 | 2.08028 |
| H | 1.81102 | 1.59229 | -0.74511 |
| O | -3.27208 | 0.66262 | 0.04544 |
| O | -2.42640 | 3.18179 | -0.06121 |
| C | -1.99417 | 4.52748 | -0.11686 |
| H | -2.88289 | 5.13545 | 0.03837 |
| H | -1.26303 | 4.73984 | 0.66893 |
| H | -1.55776 | 4.76109 | -1.09262 |
| C | -3.66875 | 0.76280 | 1.41204 |
| H | -3.12420 | 0.03181 | 2.01696 |
| H | -3.48575 | 1.77169 | 1.78928 |
| H | -4.73470 | 0.54312 | 1.44322 |
| I | -1.80096 | -2.13112 | -0.14322 |
| H | 4.99224 | -0.14409 | 2.87303 |




S1 S11

**SM (Before SET): S1** in DMSO

35

-872.3786917

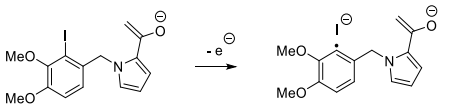
| | | | |
|---|---|---|---|
| C | -1.91698 | 0.82802 | -0.18954 |
| C | -0.95730 | -0.16843 | -0.32191 |
| C | 0.39208 | 0.12040 | -0.55173 |
| C | 0.74493 | 1.46228 | -0.64512 |
| C | -0.19235 | 2.48490 | -0.51601 |
| C | -1.52772 | 2.17678 | -0.28699 |
| H | 0.13290 | 3.51309 | -0.59590 |
| C | 1.42824 | -0.97997 | -0.69660 |
| H | 1.34273 | -1.67609 | 0.13535 |
| H | 1.26609 | -1.52389 | -1.63125 |
| N | 2.78564 | -0.46726 | -0.71240 |
| C | 3.46846 | -0.15929 | -1.86233 |
| C | 3.46148 | 0.03806 | 0.37796 |
| C | 4.61472 | 0.51854 | -1.51768 |
| H | 3.07869 | -0.45706 | -2.82389 |
| C | 4.60953 | 0.64274 | -0.10068 |
| H | 5.37018 | 1.09744 | 0.51568 |
| H | 5.37494 | 0.86331 | -2.20182 |
| C | 2.95968 | -0.12347 | 1.78702 |
| C | 3.18411 | 0.93112 | 2.63689 |
| H | 3.64783 | 1.84399 | 2.28747 |
| H | 2.89139 | 0.85871 | 3.67891 |
| O | 2.37921 | -1.23468 | 2.07293 |
| H | 1.78371 | 1.72167 | -0.81818 |
| O | -3.23265 | 0.52799 | 0.00496 |
| O | -2.52328 | 3.08368 | -0.14482 |
| C | -2.16929 | 4.45827 | -0.21474 |
| H | -3.09328 | 5.01183 | -0.06891 |
| H | -1.45670 | 4.71718 | 0.57258 |
| H | -1.74520 | 4.70241 | -1.19213 |
| C | -3.64465 | 0.64846 | 1.37072 |
| H | -3.06946 | -0.04008 | 1.99596 |
| H | -3.51057 | 1.67441 | 1.71876 |
| H | -4.69868 | 0.38005 | 1.40153 |
| I | -1.63264 | -2.18307 | -0.17108 |

**Prod (After SET): S11** in DMSO

35

-872.4892911

| | | | |
|---|---|---|---|
| C | -1.08704 | 2.26190 | 0.48439 |
| C | -0.59231 | 1.01688 | 0.77266 |
| C | 0.57883 | 0.46276 | 0.29322 |
| C | 1.32010 | 1.27631 | -0.55819 |
| C | 0.88003 | 2.56415 | -0.88929 |
| C | -0.30999 | 3.07006 | -0.37948 |
| H | 1.48286 | 3.16636 | -1.55556 |
| C | 1.00076 | -0.93632 | 0.69742 |
| H | 1.34685 | -0.94295 | 1.73038 |
| H | 0.14309 | -1.60658 | 0.60349 |
| N | 2.07512 | -1.45586 | -0.13124 |
| C | 1.85342 | -2.02077 | -1.36116 |
| C | 3.42374 | -1.22689 | 0.03762 |
| C | 3.06687 | -2.19378 | -1.98578 |
| H | 0.84626 | -2.24836 | -1.67841 |
| C | 4.06025 | -1.69210 | -1.09948 |
| H | 5.12896 | -1.69250 | -1.25149 |
| H | 3.22154 | -2.64817 | -2.95272 |
| C | 3.99995 | -0.61683 | 1.28684 |
| C | 5.06190 | 0.23620 | 1.11274 |
| H | 5.42040 | 0.49084 | 0.12417 |
| H | 5.55810 | 0.66690 | 1.97583 |
| O | 3.46246 | -0.95858 | 2.40414 |
| H | 2.25171 | 0.90642 | -0.97486 |
| O | -2.25114 | 2.76706 | 0.95720 |
| O | -0.81554 | 4.30073 | -0.64774 |
| C | -0.06587 | 5.13610 | -1.51674 |
| H | -0.62683 | 6.06369 | -1.59953 |
| H | 0.92458 | 5.34212 | -1.10195 |
| H | 0.03792 | 4.67983 | -2.50488 |
| C | -2.98887 | 1.89200 | 1.80588 |
| H | -3.26059 | 0.97670 | 1.27288 |
| H | -2.40129 | 1.63295 | 2.69137 |
| H | -3.88254 | 2.43726 | 2.09982 |
| I | -2.92630 | -2.09972 | -0.18627 |




S1 S11

**SM (Before SET): S1** in Benzene

35

-872.3354944

| | | | |
|---|---|---|---|
| C | -1.94488 | 0.84280 | -0.19539 |
| C | -0.99372 | -0.16696 | -0.26785 |
| C | 0.37014 | 0.09720 | -0.42698 |
| C | 0.74922 | 1.43234 | -0.50621 |
| C | -0.17846 | 2.46843 | -0.42933 |
| C | -1.52805 | 2.18264 | -0.27283 |
| H | 0.16959 | 3.49066 | -0.48625 |
| C | 1.39519 | -1.02021 | -0.48772 |
| H | 1.38430 | -1.57867 | 0.44930 |
| H | 1.15657 | -1.69539 | -1.31416 |
| N | 2.74413 | -0.53057 | -0.69210 |
| C | 3.28580 | -0.31500 | -1.93487 |
| C | 3.56030 | 0.01740 | 0.27489 |
| C | 4.48057 | 0.34770 | -1.77566 |
| H | 2.77368 | -0.65922 | -2.82051 |
| C | 4.65393 | 0.55489 | -0.37954 |
| H | 5.49516 | 1.01775 | 0.11279 |
| H | 5.15896 | 0.62460 | -2.56826 |
| C | 3.22070 | -0.04045 | 1.74449 |
| C | 3.62733 | 1.03658 | 2.49537 |
| H | 4.11390 | 1.88880 | 2.03972 |
| H | 3.45416 | 1.03984 | 3.56546 |
| O | 2.59592 | -1.08077 | 2.14812 |
| H | 1.80078 | 1.67308 | -0.61590 |
| O | -3.27549 | 0.56453 | -0.07377 |
| O | -2.51772 | 3.11109 | -0.18109 |
| C | -2.13042 | 4.47174 | -0.21882 |
| H | -3.04791 | 5.04767 | -0.12022 |
| H | -1.45523 | 4.71151 | 0.60782 |
| H | -1.64612 | 4.71706 | -1.16856 |
| C | -3.75468 | 0.68712 | 1.26515 |
| H | -3.21720 | -0.00298 | 1.92210 |
| H | -3.63401 | 1.71283 | 1.62066 |
| H | -4.81088 | 0.42407 | 1.24176 |
| I | -1.70197 | -2.17045 | -0.11463 |

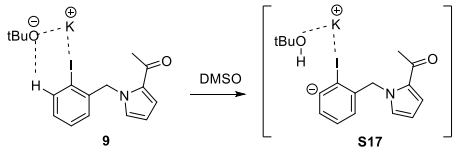
**Prod (After SET): S11** in Benzene

35

-872.3823971

| | | | |
|---|---|---|---|
| C | -0.66226 | 2.34181 | 0.15912 |
| C | -0.29479 | 1.08633 | -0.25676 |
| C | -1.11607 | 0.13163 | -0.81844 |
| C | -2.45258 | 0.49501 | -0.97132 |
| C | -2.89642 | 1.75859 | -0.56768 |
| C | -2.02207 | 2.68372 | -0.00536 |
| H | -3.94198 | 2.00612 | -0.69165 |
| C | -0.61422 | -1.24545 | -1.19209 |
| H | -1.19921 | -1.64088 | -2.01953 |
| H | 0.44457 | -1.19685 | -1.45339 |
| N | -0.73706 | -2.17794 | -0.07427 |
| C | 0.27922 | -2.40499 | 0.81608 |
| C | -1.89377 | -2.78561 | 0.36429 |
| C | -0.20798 | -3.19900 | 1.83032 |
| H | 1.25711 | -1.97364 | 0.64788 |
| C | -1.57900 | -3.44112 | 1.54236 |
| H | -2.26957 | -4.04914 | 2.10688 |
| H | 0.36415 | -3.57297 | 2.66585 |
| C | -3.19876 | -2.71626 | -0.38875 |
| C | -4.34173 | -2.72148 | 0.37811 |
| H | -4.29572 | -2.71453 | 1.45893 |
| H | -5.31119 | -2.72091 | -0.10827 |
| O | -3.13496 | -2.65714 | -1.66642 |
| H | -3.14517 | -0.22981 | -1.38944 |
| O | 0.17372 | 3.25558 | 0.70842 |
| O | -2.37362 | 3.93256 | 0.41790 |
| C | -3.73681 | 4.28309 | 0.31466 |
| H | -3.82144 | 5.29088 | 0.71705 |
| H | -4.07091 | 4.27749 | -0.72784 |
| H | -4.36556 | 3.60287 | 0.89792 |
| C | 1.52033 | 2.80974 | 0.85166 |
| H | 1.56930 | 1.91590 | 1.47928 |
| H | 1.95979 | 2.56674 | -0.11891 |
| H | 2.06331 | 3.62882 | 1.31886 |
| I | 3.99816 | -0.16318 | -0.23170 |

## 3. Benzyne Pathway




9 S17

**SM: 9** + KOtBu in DMSO
43
-1476.8731516

| | | | |
|---|---|---|---|
| C | -0.67449 | 2.75628 | -0.42616 |
| C | -1.68164 | 1.81817 | -0.62197 |
| C | -1.39262 | 0.45361 | -0.70260 |
| C | -0.05554 | 0.07237 | -0.58163 |
| C | 0.96975 | 0.98965 | -0.38285 |
| C | 0.64685 | 2.34278 | -0.30475 |
| H | -0.92600 | 3.80848 | -0.36862 |
| H | -2.71107 | 2.14809 | -0.71349 |
| H | 2.00837 | 0.65795 | -0.28937 |
| H | 1.43645 | 3.07000 | -0.15135 |
| C | -2.49906 | -0.55905 | -0.93123 |
| H | -2.47909 | -0.89888 | -1.96957 |
| H | -2.34912 | -1.44269 | -0.31481 |
| N | -3.82555 | -0.01266 | -0.68849 |
| C | -4.62598 | 0.41655 | -1.70131 |
| C | -4.38399 | 0.38682 | 0.51857 |
| C | -5.72180 | 1.07063 | -1.17247 |
| H | -4.34972 | 0.22617 | -2.72739 |
| C | -5.56523 | 1.05376 | 0.22518 |
| H | -6.23590 | 1.45524 | 0.96863 |
| H | -6.53550 | 1.49708 | -1.73682 |
| C | -3.88226 | 0.14553 | 1.88227 |
| C | -2.72383 | -0.78564 | 2.14624 |
| H | -1.80096 | -0.39684 | 1.70817 |
| H | -2.59613 | -0.87129 | 3.22352 |
| O | -4.44374 | 0.69664 | 2.81558 |
| I | 0.49833 | -1.99167 | -0.70851 |
| H | -2.91543 | -1.77471 | 1.72470 |
| O | 3.97600 | -0.00846 | 0.09901 |
| C | 4.78869 | 1.06840 | -0.18692 |
| C | 4.61798 | 2.16699 | 0.88532 |
| H | 5.22619 | 3.05600 | 0.68518 |
| H | 3.56646 | 2.46944 | 0.93286 |
| H | 4.90153 | 1.77030 | 1.86619 |
| C | 4.44064 | 1.67882 | -1.56113 |
| H | 3.40146 | 2.02203 | -1.56734 |
| H | 5.08365 | 2.52809 | -1.81720 |
| H | 4.55037 | 0.91541 | -2.33766 |
| C | 6.27323 | 0.65075 | -0.21287 |
| H | 6.94185 | 1.49140 | -0.42952 |
| H | 6.55258 | 0.22707 | 0.75697 |
| H | 6.42503 | -0.11759 | -0.97736 |
| K | 2.93316 | -0.84513 | 2.17672 |

**TS: 9** + KOtBu in DMSO
43
-1476.8560648

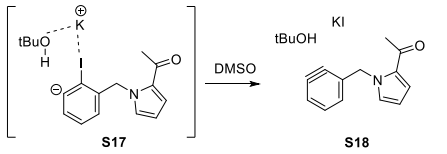
| | | | |
|---|---|---|---|
| C | -0.52224 | 2.72389 | -0.54108 |
| C | -1.53972 | 1.79061 | -0.72195 |
| C | -1.25405 | 0.42414 | -0.72744 |
| C | 0.08793 | 0.07162 | -0.54975 |
| C | 1.14740 | 0.93524 | -0.36031 |
| C | 0.78910 | 2.29653 | -0.36000 |
| H | -0.76292 | 3.78184 | -0.53931 |
| H | -2.56392 | 2.12282 | -0.85666 |
| H | 2.51379 | 0.52719 | -0.19922 |
| H | 1.56277 | 3.04834 | -0.21566 |
| C | -2.35862 | -0.59586 | -0.92768 |
| H | -2.31732 | -0.99635 | -1.94345 |
| H | -2.22836 | -1.44249 | -0.25805 |
| N | -3.69120 | -0.03583 | -0.74796 |
| C | -4.46948 | 0.33113 | -1.80031 |
| C | -4.28216 | 0.42043 | 0.42199 |
| C | -5.58392 | 1.00248 | -1.33364 |
| H | -4.16682 | 0.08811 | -2.80766 |
| C | -5.46182 | 1.06037 | 0.06609 |
| H | -6.15325 | 1.49401 | 0.77160 |
| H | -6.38694 | 1.38972 | -1.93995 |
| C | -3.80946 | 0.25797 | 1.80710 |
| C | -2.64847 | -0.64533 | 2.14670 |
| H | -1.72169 | -0.27882 | 1.69754 |
| H | -2.53798 | -0.66362 | 3.22909 |
| O | -4.39732 | 0.85143 | 2.69792 |
| I | 0.57181 | -2.07649 | -0.56551 |
| H | -2.82785 | -1.65986 | 1.78409 |
| O | 3.60719 | 0.11525 | 0.03548 |
| C | 4.61365 | 1.06354 | -0.23121 |
| C | 4.58927 | 2.16580 | 0.83757 |
| H | 5.35015 | 2.92960 | 0.65160 |
| H | 3.60936 | 2.65208 | 0.85409 |
| H | 4.77406 | 1.73249 | 1.82533 |
| C | 4.40404 | 1.68981 | -1.61688 |
| H | 3.44552 | 2.21420 | -1.65906 |
| H | 5.19889 | 2.40309 | -1.85310 |
| H | 4.40028 | 0.90774 | -2.38134 |
| C | 5.96659 | 0.35026 | -0.19466 |
| H | 6.78972 | 1.04655 | -0.38075 |
| H | 6.11734 | -0.11223 | 0.78469 |
| H | 5.99549 | -0.43468 | -0.95512 |
| K | 2.40816 | -0.53864 | 2.22339 |

**Prod: S17** + $K^+$ + HOtBu in DMSO

43

-1476.8579160

| | | | |
|---|---|---|---|
| C | -0.50431 | 2.73422 | -0.08616 |
| C | -1.52135 | 1.84009 | -0.41436 |
| C | -1.24270 | 0.47995 | -0.55945 |
| C | 0.09188 | 0.11051 | -0.36154 |
| C | 1.15585 | 0.91444 | -0.03740 |
| C | 0.79612 | 2.27379 | 0.09865 |
| H | -0.73729 | 3.78859 | 0.02362 |
| H | -2.53614 | 2.19747 | -0.55568 |
| H | 2.84821 | 0.41511 | -0.14661 |
| H | 1.56262 | 3.00514 | 0.35296 |
| C | -2.33688 | -0.50437 | -0.92366 |
| H | -2.20800 | -0.83940 | -1.95567 |
| H | -2.27851 | -1.39632 | -0.30394 |
| N | -3.67492 | 0.06446 | -0.83006 |
| C | -4.33462 | 0.53573 | -1.92056 |
| C | -4.39160 | 0.41133 | 0.30688 |
| C | -5.49456 | 1.16994 | -1.51645 |
| H | -3.92396 | 0.38612 | -2.90779 |
| C | -5.52697 | 1.09203 | -0.11321 |
| H | -6.28985 | 1.46580 | 0.55147 |
| H | -6.22642 | 1.62117 | -2.16711 |
| C | -4.06782 | 0.12770 | 1.71493 |
| C | -2.90834 | -0.75888 | 2.09970 |
| H | -1.96154 | -0.35267 | 1.73580 |
| H | -2.87951 | -0.82785 | 3.18527 |
| O | -4.77681 | 0.61019 | 2.58451 |
| I | 0.54823 | -2.06175 | -0.61945 |
| H | -3.03573 | -1.75924 | 1.67916 |
| O | 3.80621 | 0.04365 | -0.11275 |
| C | 4.73168 | 1.11415 | -0.28104 |
| C | 4.69866 | 2.01978 | 0.95350 |
| H | 5.38799 | 2.86088 | 0.84307 |
| H | 3.69049 | 2.41705 | 1.10262 |
| H | 4.98771 | 1.45519 | 1.84455 |
| C | 4.36954 | 1.91915 | -1.53118 |
| H | 3.37695 | 2.36456 | -1.42114 |
| H | 5.09349 | 2.72069 | -1.69890 |
| H | 4.36164 | 1.26697 | -2.40819 |
| C | 6.11080 | 0.48418 | -0.43720 |
| H | 6.87741 | 1.25411 | -0.55519 |
| H | 6.35293 | -0.11597 | 0.44356 |
| H | 6.12977 | -0.16466 | -1.31618 |
| K | 2.53097 | -0.73445 | 2.13646 |




**S17** **S18**

**TS** (CI bond cleavage)**: S17** in DMSO

43

-1476.8462671

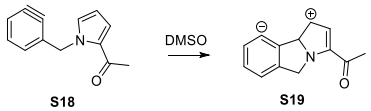
| | | | |
|---|---|---|---|
| C | 0.68040 | -2.98420 | -0.71942 |
| C | 1.65163 | -1.98216 | -0.85283 |
| C | 1.32378 | -0.61631 | -0.82083 |
| C | -0.03715 | -0.48877 | -0.64475 |
| C | -1.00144 | -1.30853 | -0.51639 |
| C | -0.67053 | -2.67785 | -0.54749 |
| H | 0.99433 | -4.02208 | -0.75115 |
| H | 2.69412 | -2.25932 | -0.98211 |
| H | -2.90698 | -0.48009 | -0.42882 |
| H | -1.40677 | -3.46828 | -0.44441 |
| C | 2.33776 | 0.48939 | -0.97154 |
| H | 2.30495 | 0.88310 | -1.98951 |
| H | 2.08855 | 1.31720 | -0.31312 |
| N | 3.69712 | 0.02810 | -0.73161 |
| C | 4.55034 | -0.26881 | -1.74853 |
| C | 4.25690 | -0.41066 | 0.46044 |
| C | 5.68139 | -0.87312 | -1.23443 |
| H | 4.28330 | -0.02947 | -2.76681 |
| C | 5.49222 | -0.96526 | 0.15640 |
| H | 6.17570 | -1.36363 | 0.88991 |
| H | 6.53935 | -1.19356 | -1.80357 |
| C | 3.70880 | -0.29035 | 1.82195 |
| C | 2.50766 | 0.57634 | 2.11400 |
| H | 1.60802 | 0.17592 | 1.63908 |
| H | 2.35939 | 0.59973 | 3.19178 |
| O | 4.26904 | -0.88144 | 2.73146 |
| I | -0.66366 | 2.37522 | -0.51458 |
| H | 2.66250 | 1.59263 | 1.74526 |
| O | -3.72955 | -0.12639 | -0.04063 |
| C | -4.73027 | -1.15655 | -0.12646 |
| C | -4.41771 | -2.24989 | 0.89422 |
| H | -5.14509 | -3.06220 | 0.82533 |
| H | -3.42108 | -2.66363 | 0.71566 |
| H | -4.45208 | -1.84529 | 1.90913 |
| C | -4.73453 | -1.72829 | -1.54180 |
| H | -3.76897 | -2.19222 | -1.76736 |
| H | -5.51178 | -2.48805 | -1.64933 |
| H | -4.91771 | -0.93434 | -2.26933 |
| C | -6.05433 | -0.47897 | 0.19460 |
| H | -6.86821 | -1.20690 | 0.17673 |
| H | -6.01391 | -0.02620 | 1.18811 |
| H | -6.26593 | 0.30236 | -0.53848 |
| K | -2.06962 | 0.46462 | 2.04148 |

**Prod** (CI bond cleavage)**: S18** + KI + HOtBu in DMSO

43

-1476.8508356

| | | | |
|---|---|---|---|
| C | 1.95681 | 1.64693 | 2.74714 |
| C | 2.34921 | 0.67198 | 1.81448 |
| C | 1.49113 | -0.35613 | 1.37667 |
| C | 0.26539 | -0.20509 | 1.99851 |
| C | -0.11765 | 0.63909 | 2.82883 |
| C | 0.67559 | 1.67264 | 3.31746 |
| H | 2.67497 | 2.40664 | 3.03695 |
| H | 3.35941 | 0.70659 | 1.41525 |
| H | -1.64835 | 0.82110 | 0.52838 |
| H | 0.37825 | 2.42450 | 4.03705 |
| C | 1.90704 | -1.45420 | 0.43048 |
| H | 2.18902 | -2.33964 | 1.00431 |
| H | 1.06901 | -1.74501 | -0.19890 |
| N | 3.06686 | -1.07626 | -0.36658 |
| C | 4.33036 | -1.45848 | -0.03111 |
| C | 3.14780 | -0.06716 | -1.31459 |
| C | 5.23943 | -0.73623 | -0.77870 |
| H | 4.48443 | -2.21166 | 0.72689 |
| C | 4.49165 | 0.14580 | -1.58244 |
| H | 4.86262 | 0.84557 | -2.31524 |
| H | 6.31144 | -0.84808 | -0.74908 |
| C | 2.03504 | 0.60894 | -2.00082 |
| C | 0.65102 | 0.00968 | -1.99786 |
| H | 0.18049 | 0.10610 | -1.01451 |
| H | 0.04385 | 0.54951 | -2.72372 |
| O | 2.26053 | 1.63812 | -2.61732 |
| I | -1.86645 | -2.31136 | 0.38187 |
| H | 0.68193 | -1.05162 | -2.25433 |
| O | -2.07256 | 1.32339 | -0.18223 |
| C | -1.75013 | 2.72198 | -0.05807 |
| C | -0.23848 | 2.90823 | -0.16790 |
| H | 0.02674 | 3.95742 | -0.01574 |
| H | 0.28109 | 2.31282 | 0.58941 |
| H | 0.11449 | 2.60354 | -1.15559 |
| C | -2.27466 | 3.24316 | 1.27706 |
| H | -1.78323 | 2.73118 | 2.10843 |
| H | -2.08049 | 4.31395 | 1.37213 |
| H | -3.35148 | 3.07460 | 1.34934 |
| C | -2.46157 | 3.40051 | -1.22038 |
| H | -2.26638 | 4.47458 | -1.20795 |
| H | -2.10383 | 2.99615 | -2.17100 |
| H | -3.54078 | 3.24316 | -1.15067 |
| K | -3.37479 | -0.17776 | -1.91160 |




S18 S19

**SM: S18** in DMSO

26

-631.7536745

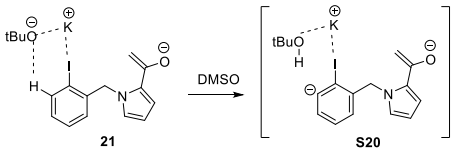
| | | | |
|---|---|---|---|
| C | -3.01287 | -1.27646 | -0.51769 |
| C | -1.85308 | -1.13014 | 0.26223 |
| C | -1.37796 | 0.11691 | 0.70491 |
| C | -2.21787 | 1.13823 | 0.26880 |
| C | -3.23298 | 0.97641 | -0.42418 |
| C | -3.79910 | -0.18186 | -0.91685 |
| H | -3.31741 | -2.27149 | -0.82319 |
| H | -1.30519 | -2.02401 | 0.54265 |
| H | -4.69391 | -0.28250 | -1.51428 |
| C | -0.12786 | 0.29048 | 1.52861 |
| H | -0.30079 | 1.00745 | 2.33102 |
| H | 0.16472 | -0.65277 | 1.98126 |
| N | 0.96869 | 0.81642 | 0.71169 |
| C | 1.06354 | 2.15168 | 0.45138 |
| C | 1.71814 | 0.13084 | -0.23404 |
| C | 1.90419 | 2.34983 | -0.62395 |
| H | 0.50515 | 2.85940 | 1.04563 |
| C | 2.31083 | 1.07228 | -1.06023 |
| H | 3.00823 | 0.83645 | -1.84914 |
| H | 2.20151 | 3.30468 | -1.02709 |
| C | 2.01950 | -1.30928 | -0.26887 |
| C | 1.91824 | -2.14882 | 0.98423 |
| H | 0.91164 | -2.56216 | 1.08422 |
| H | 2.61058 | -2.98354 | 0.88577 |
| O | 2.42566 | -1.80643 | -1.30577 |
| H | 2.15301 | -1.57574 | 1.88144 |

**TS: S18** in DMSO
26
-631.7310143

| | | | |
|---|---|---|---|
| C | -3.51929 | -1.07893 | -0.61996 |
| C | -2.35453 | -1.61168 | -0.04649 |
| C | -1.34671 | -0.75188 | 0.37484 |
| C | -1.62566 | 0.59220 | 0.16395 |
| C | -2.66950 | 1.16721 | -0.33876 |
| C | -3.69214 | 0.30019 | -0.77411 |
| H | -4.29982 | -1.75685 | -0.95086 |
| H | -2.23820 | -2.68446 | 0.06542 |
| H | -4.61227 | 0.66726 | -1.21986 |
| C | -0.01640 | -1.06931 | 1.01909 |
| H | -0.12167 | -1.30425 | 2.08064 |
| H | 0.49908 | -1.88785 | 0.52409 |
| N | 0.72969 | 0.18819 | 0.86528 |
| C | -0.03795 | 1.35344 | 1.01324 |
| C | 1.71981 | 0.43397 | -0.02912 |
| C | 0.62150 | 2.36790 | 0.28215 |
| H | -0.56613 | 1.50387 | 1.94721 |
| C | 1.69337 | 1.79030 | -0.38068 |
| H | 2.40791 | 2.26471 | -1.03444 |
| H | 0.32257 | 3.40500 | 0.26071 |
| C | 2.73885 | -0.54281 | -0.49987 |
| C | 3.02939 | -1.78066 | 0.31007 |
| H | 2.52398 | -2.63653 | -0.14582 |
| H | 4.10166 | -1.96839 | 0.26587 |
| O | 3.36522 | -0.28125 | -1.50540 |
| H | 2.70892 | -1.68938 | 1.34713 |

**Prod: S19** in DMSO
26
-631.7485995

| | | | |
|---|---|---|---|
| C | -3.66122 | -0.98075 | -0.55156 |
| C | -2.47591 | -1.63265 | -0.20195 |
| C | -1.41511 | -0.83381 | 0.19083 |
| C | -1.56600 | 0.56068 | 0.22648 |
| C | -2.71139 | 1.28523 | -0.09927 |
| C | -3.75646 | 0.41513 | -0.50187 |
| H | -4.51535 | -1.57149 | -0.87014 |
| H | -2.38882 | -2.71264 | -0.24388 |
| H | -4.71613 | 0.84028 | -0.79659 |
| C | -0.02704 | -1.27683 | 0.61276 |
| H | 0.00453 | -1.70057 | 1.61956 |
| H | 0.44684 | -1.96145 | -0.08741 |
| N | 0.67351 | 0.02484 | 0.60782 |
| C | -0.25746 | 1.14055 | 0.77759 |
| C | 1.77477 | 0.43365 | 0.05036 |
| C | 0.48856 | 2.27750 | 0.19235 |
| H | -0.36794 | 1.32911 | 1.85877 |
| C | 1.71593 | 1.85951 | -0.18393 |
| H | 2.52673 | 2.42944 | -0.60952 |
| H | 0.10216 | 3.28605 | 0.16309 |
| C | 2.94532 | -0.44429 | -0.35214 |
| C | 3.13576 | -1.77356 | 0.31330 |
| H | 2.64342 | -2.54486 | -0.28609 |
| H | 4.20092 | -1.99700 | 0.34013 |
| O | 3.68678 | 0.00498 | -1.18741 |
| H | 2.71636 | -1.79277 | 1.31883 |




**SM: 21** + KOtBu in DMSO

42

-1476.3702982

| | | | |
|---|---|---|---|
| C | 0.68359 | -2.62655 | -0.97128 |
| C | 1.70437 | -1.68371 | -0.97059 |
| C | 1.43337 | -0.31930 | -0.83165 |
| C | 0.09609 | 0.05300 | -0.69931 |
| C | -0.94507 | -0.86901 | -0.68538 |
| C | -0.63831 | -2.22067 | -0.82392 |
| H | 0.92304 | -3.67753 | -1.08137 |
| H | 2.73666 | -2.00311 | -1.07055 |
| H | -1.98133 | -0.54777 | -0.55257 |
| H | -1.43982 | -2.95108 | -0.81554 |
| C | 2.56298 | 0.69262 | -0.84567 |
| H | 2.63537 | 1.15305 | -1.83497 |
| H | 2.35528 | 1.48250 | -0.12998 |
| N | 3.85231 | 0.09288 | -0.54985 |
| C | 4.76621 | -0.22625 | -1.52606 |
| C | 4.21082 | -0.52117 | 0.63439 |
| C | 5.73829 | -1.02215 | -0.96843 |
| H | 4.63828 | 0.14041 | -2.53301 |
| C | 5.38079 | -1.21451 | 0.39431 |
| H | 5.92300 | -1.77898 | 1.13743 |
| H | 6.60662 | -1.41004 | -1.47845 |
| C | 3.44274 | -0.44173 | 1.92999 |
| C | 2.97081 | 0.78527 | 2.32836 |
| H | 2.43121 | 0.87857 | 3.26489 |
| O | 3.33158 | -1.54788 | 2.57103 |
| I | -0.43935 | 2.12085 | -0.51434 |
| H | 3.18785 | 1.68696 | 1.77094 |
| O | -3.93315 | 0.01263 | 0.18001 |
| C | -4.74781 | -1.03392 | -0.19771 |
| C | -4.46074 | -2.27700 | 0.67273 |
| H | -5.06771 | -3.14442 | 0.39067 |
| H | -3.40387 | -2.54915 | 0.58248 |
| H | -4.66161 | -2.04383 | 1.72388 |
| C | -4.51571 | -1.41899 | -1.67481 |
| H | -3.47603 | -1.72574 | -1.82531 |
| H | -5.16525 | -2.23940 | -1.99909 |
| H | -4.70885 | -0.55132 | -2.31362 |
| C | -6.23648 | -0.66607 | -0.03225 |
| H | -6.90501 | -1.48625 | -0.31683 |
| H | -6.43608 | -0.40387 | 1.01148 |
| H | -6.47186 | 0.20365 | -0.65359 |
| K | -2.59283 | 0.53974 | 2.18040 |

**TS: 21** + KOtBu in DMSO

42

-1476.3517258

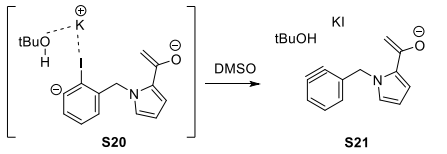
| | | | |
|---|---|---|---|
| C | 0.55168 | -2.65323 | -0.71792 |
| C | 1.56919 | -1.70605 | -0.79970 |
| C | 1.27995 | -0.34296 | -0.71019 |
| C | -0.06974 | -0.01448 | -0.54975 |
| C | -1.13193 | -0.88881 | -0.45076 |
| C | -0.76687 | -2.24569 | -0.53944 |
| H | 0.79725 | -3.70800 | -0.78777 |
| H | 2.60068 | -2.01958 | -0.92370 |
| H | -2.51040 | -0.49049 | -0.25878 |
| H | -1.53983 | -3.00906 | -0.46790 |
| C | 2.38330 | 0.69356 | -0.80107 |
| H | 2.33513 | 1.20361 | -1.76734 |
| H | 2.24009 | 1.44440 | -0.02964 |
| N | 3.71402 | 0.12199 | -0.68029 |
| C | 4.48643 | -0.18510 | -1.77433 |
| C | 4.25535 | -0.46911 | 0.44405 |
| C | 5.54995 | -0.95026 | -1.35742 |
| H | 4.20376 | 0.16524 | -2.75520 |
| C | 5.39710 | -1.13583 | 0.04389 |
| H | 6.05176 | -1.68099 | 0.70671 |
| H | 6.34520 | -1.32147 | -1.98547 |
| C | 3.68276 | -0.40183 | 1.83750 |
| C | 3.24454 | 0.81446 | 2.30163 |
| H | 2.84262 | 0.89768 | 3.30576 |
| O | 3.69667 | -1.50793 | 2.48898 |
| I | -0.56783 | 2.13476 | -0.44844 |
| H | 3.35130 | 1.71857 | 1.71697 |
| O | -3.59238 | -0.10225 | 0.02022 |
| C | -4.59252 | -1.05037 | -0.27263 |
| C | -4.52512 | -2.20784 | 0.73420 |
| H | -5.28184 | -2.97063 | 0.52834 |
| H | -3.53937 | -2.68066 | 0.69586 |
| H | -4.68707 | -1.83040 | 1.74848 |
| C | -4.40884 | -1.59786 | -1.69465 |
| H | -3.44363 | -2.10303 | -1.78792 |
| H | -5.19851 | -2.31070 | -1.94904 |
| H | -4.43647 | -0.77622 | -2.41587 |
| C | -5.95300 | -0.35953 | -0.16448 |
| H | -6.77136 | -1.05695 | -0.36680 |
| H | -6.08521 | 0.04905 | 0.84110 |
| H | -6.01178 | 0.46377 | -0.88135 |
| K | -2.30070 | 0.37402 | 2.21663 |

**Prod: S20** + $K^+$ + HOtBu in DMSO

42

-1476.3532145

| | | | |
|---|---|---|---|
| C | -0.51262 | 2.70532 | -0.21595 |
| C | -1.53955 | 1.78997 | -0.44011 |
| C | -1.26108 | 0.42484 | -0.53063 |
| C | 0.08612 | 0.07854 | -0.38538 |
| C | 1.16093 | 0.89925 | -0.15651 |
| C | 0.79967 | 2.26287 | -0.07426 |
| H | -0.74703 | 3.76339 | -0.15080 |
| H | -2.56534 | 2.12942 | -0.54199 |
| H | 2.83792 | 0.40189 | -0.19328 |
| H | 1.57276 | 3.01039 | 0.10169 |
| C | -2.36511 | -0.58666 | -0.77601 |
| H | -2.22059 | -1.06521 | -1.74821 |
| H | -2.31566 | -1.36437 | -0.01818 |
| N | -3.69362 | 0.00253 | -0.77410 |
| C | -4.27323 | 0.49701 | -1.91780 |
| C | -4.39175 | 0.45907 | 0.32673 |
| C | -5.36838 | 1.24850 | -1.56402 |
| H | -3.84527 | 0.27525 | -2.88363 |
| C | -5.43688 | 1.23008 | -0.14382 |
| H | -6.17849 | 1.70383 | 0.48114 |
| H | -6.04437 | 1.74043 | -2.24658 |
| C | -4.06604 | 0.15794 | 1.76787 |
| C | -3.75863 | -1.13701 | 2.10673 |
| H | -3.54320 | -1.38866 | 3.13982 |
| O | -4.15302 | 1.15691 | 2.56943 |
| I | 0.54516 | -2.10920 | -0.57079 |
| H | -3.79208 | -1.93775 | 1.37954 |
| O | 3.80017 | 0.03678 | -0.09466 |
| C | 4.72921 | 1.10397 | -0.25684 |
| C | 4.63103 | 2.05819 | 0.93732 |
| H | 5.31689 | 2.90189 | 0.82473 |
| H | 3.61341 | 2.44949 | 1.02510 |
| H | 4.88522 | 1.53337 | 1.86273 |
| C | 4.43037 | 1.85757 | -1.55497 |
| H | 3.43146 | 2.30056 | -1.51490 |
| H | 5.15903 | 2.65608 | -1.71682 |
| H | 4.47077 | 1.17091 | -2.40433 |
| C | 6.11770 | 0.47753 | -0.31575 |
| H | 6.88609 | 1.24717 | -0.42450 |
| H | 6.31567 | -0.08459 | 0.60041 |
| H | 6.18584 | -0.20644 | -1.16511 |
| K | 2.44586 | -0.64099 | 2.13820 |




**TS** (CI bond cleavage)**: S20** in DMSO

42

-1476.3437007

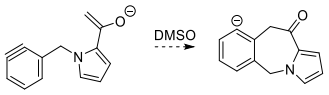
| | | | |
|---|---|---|---|
| C | 0.68858 | -2.87018 | -0.73413 |
| C | 1.66660 | -1.87105 | -0.81957 |
| C | 1.34422 | -0.50676 | -0.73441 |
| C | -0.01851 | -0.37650 | -0.57039 |
| C | -1.00517 | -1.19029 | -0.47857 |
| C | -0.65957 | -2.55723 | -0.55930 |
| H | 0.99428 | -3.90887 | -0.80368 |
| H | 2.71125 | -2.14191 | -0.94469 |
| H | -2.87983 | -0.46875 | -0.39995 |
| H | -1.39961 | -3.34921 | -0.49049 |
| C | 2.36860 | 0.59646 | -0.82866 |
| H | 2.29673 | 1.08048 | -1.80582 |
| H | 2.15047 | 1.34758 | -0.07630 |
| N | 3.72610 | 0.10223 | -0.67983 |
| C | 4.53300 | -0.16739 | -1.75967 |
| C | 4.27403 | -0.46333 | 0.45544 |
| C | 5.62355 | -0.88022 | -1.32208 |
| H | 4.25249 | 0.16997 | -2.74564 |
| C | 5.45343 | -1.07393 | 0.07628 |
| H | 6.12230 | -1.58611 | 0.75105 |
| H | 6.44840 | -1.21128 | -1.93427 |
| C | 3.67382 | -0.42072 | 1.83806 |
| C | 3.15088 | 0.76905 | 2.28244 |
| H | 2.72904 | 0.83562 | 3.27953 |
| O | 3.74648 | -1.51800 | 2.50019 |
| I | -0.64425 | 2.39373 | -0.43926 |
| H | 3.20926 | 1.67300 | 1.69076 |
| O | -3.74228 | -0.13029 | -0.07759 |
| C | -4.70014 | -1.19353 | -0.20824 |
| C | -4.42053 | -2.25839 | 0.85206 |
| H | -5.12057 | -3.09208 | 0.75851 |
| H | -3.40424 | -2.64720 | 0.74071 |
| H | -4.52649 | -1.83383 | 1.85387 |
| C | -4.59327 | -1.79257 | -1.60896 |
| H | -3.60047 | -2.22756 | -1.76105 |
| H | -5.33818 | -2.57902 | -1.75000 |
| H | -4.75350 | -1.01893 | -2.36346 |
| C | -6.06641 | -0.55964 | 0.01030 |
| H | -6.85162 | -1.31611 | -0.05493 |
| H | -6.11329 | -0.09356 | 0.99739 |
| H | -6.25273 | 0.20506 | -0.74699 |
| K | -2.13279 | 0.45596 | 2.05898 |

**Prod** (CI bond cleavage)**: S21** + KI + HOtBu in DMSO

42

-1476.3410468

| | | | |
|---|---|---|---|
| C | -1.31533 | 3.15966 | -1.08685 |
| C | -2.08264 | 1.98407 | -1.09054 |
| C | -1.51779 | 0.69785 | -0.97151 |
| C | -0.15252 | 0.84781 | -0.85559 |
| C | 0.58659 | 1.85261 | -0.85553 |
| C | 0.08280 | 3.14927 | -0.95546 |
| H | -1.82643 | 4.11227 | -1.18034 |
| H | -3.16459 | 2.05631 | -1.16956 |
| H | 2.65914 | 0.29967 | -0.39226 |
| H | 0.66777 | 4.06065 | -0.94821 |
| C | -2.32659 | -0.57271 | -0.96589 |
| H | -2.40483 | -0.96310 | -1.98351 |
| H | -1.81176 | -1.31835 | -0.36838 |
| N | -3.68451 | -0.34628 | -0.49075 |
| C | -4.75456 | -0.25123 | -1.34911 |
| C | -4.05062 | 0.13501 | 0.75170 |
| C | -5.82678 | 0.25807 | -0.65697 |
| H | -4.65279 | -0.55142 | -2.38074 |
| C | -5.37612 | 0.51296 | 0.66750 |
| H | -5.95389 | 0.90552 | 1.49037 |
| H | -6.81653 | 0.41988 | -1.05566 |
| C | -3.16469 | 0.21046 | 1.96847 |
| C | -2.33032 | -0.84763 | 2.23344 |
| H | -1.70034 | -0.82803 | 3.11682 |
| O | -3.31269 | 1.26334 | 2.68784 |
| I | 1.07399 | -2.34724 | -0.74223 |
| H | -2.32218 | -1.73727 | 1.61820 |
| O | 3.40997 | 0.28277 | 0.21855 |
| C | 4.23240 | 1.44818 | 0.02346 |
| C | 3.64926 | 2.61707 | 0.81392 |
| H | 4.25161 | 3.51669 | 0.66733 |
| H | 2.62702 | 2.82301 | 0.48999 |
| H | 3.63195 | 2.37865 | 1.88039 |
| C | 4.29692 | 1.77372 | -1.46572 |
| H | 3.30117 | 2.02075 | -1.84709 |
| H | 4.95227 | 2.62939 | -1.64128 |
| H | 4.68286 | 0.91748 | -2.02388 |
| C | 5.60722 | 1.07167 | 0.56025 |
| H | 6.28803 | 1.92282 | 0.49182 |
| H | 5.53120 | 0.77200 | 1.60825 |
| H | 6.02381 | 0.24059 | -0.01255 |
| K | 2.14658 | -0.92103 | 2.24050 |




S21 S22

**SM: S21** in DMSO

25

-631.2564870

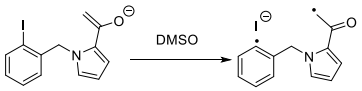
| | | | |
|---|---|---|---|
| C | 3.32120 | -0.97214 | -0.60505 |
| C | 2.18469 | -1.44545 | 0.07174 |
| C | 1.20448 | -0.57879 | 0.59012 |
| C | 1.58129 | 0.71539 | 0.31525 |
| C | 2.55163 | 1.22889 | -0.28925 |
| C | 3.54856 | 0.39469 | -0.81340 |
| H | 4.03949 | -1.69206 | -0.98328 |
| H | 2.04995 | -2.51493 | 0.20367 |
| H | 4.42771 | 0.73969 | -1.34526 |
| C | -0.03663 | -1.04047 | 1.29924 |
| H | 0.04744 | -2.10396 | 1.52074 |
| H | -0.14510 | -0.50902 | 2.24273 |
| N | -1.23637 | -0.87408 | 0.47916 |
| C | -1.95587 | -1.94860 | 0.01793 |
| C | -1.70911 | 0.28119 | -0.11494 |
| C | -2.91062 | -1.49417 | -0.86102 |
| H | -1.71456 | -2.94720 | 0.34797 |
| C | -2.74564 | -0.08723 | -0.95155 |
| H | -3.32446 | 0.60434 | -1.54403 |
| H | -3.63756 | -2.10432 | -1.37444 |
| C | -1.20868 | 1.68149 | 0.11585 |
| C | -0.79957 | 2.03543 | 1.38811 |
| H | -0.44727 | 3.04416 | 1.57094 |
| O | -1.23241 | 2.45014 | -0.90092 |
| H | -0.93594 | 1.37936 | 2.23601 |

**Prod: S22** in DMSO
25
-631.3484140

| | | | |
|---|---|---|---|
| C | 3.23835 | -1.07105 | -0.69639 |
| C | 2.09876 | -1.58257 | -0.08121 |
| C | 1.16739 | -0.69727 | 0.45654 |
| C | 1.39006 | 0.68878 | 0.37501 |
| C | 2.52023 | 1.26777 | -0.24261 |
| C | 3.42291 | 0.31240 | -0.76558 |
| H | 3.97358 | -1.75100 | -1.11856 |
| H | 1.93088 | -2.65360 | -0.01922 |
| H | 4.33254 | 0.65638 | -1.26032 |
| C | -0.07880 | -1.22839 | 1.12099 |
| H | -0.05025 | -2.31626 | 1.17857 |
| H | -0.17689 | -0.84396 | 2.14044 |
| N | -1.29650 | -0.88355 | 0.37603 |
| C | -2.22725 | -1.79045 | -0.00959 |
| C | -1.67566 | 0.36705 | -0.07775 |
| C | -3.22802 | -1.14234 | -0.71593 |
| H | -2.10783 | -2.83368 | 0.23969 |
| C | -2.87714 | 0.21831 | -0.75988 |
| H | -3.42016 | 1.02586 | -1.22583 |
| H | -4.09962 | -1.60987 | -1.14567 |
| C | -0.94095 | 1.61902 | 0.14497 |
| C | 0.32176 | 1.59748 | 0.97667 |
| H | 0.69892 | 2.61716 | 1.02257 |
| O | -1.35597 | 2.65785 | -0.34837 |
| H | 0.05216 | 1.27856 | 1.99160 |

## 4. Intramolecular Analysis of 9

### 4.1 Franck-Condon



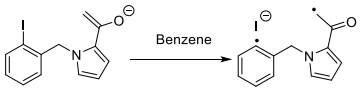

21 S23

**SM:** Singlet **21** in DMSO
27
-643.3534550

| | | | |
|---|---|---|---|
| C | -0.19425 | 3.13096 | 0.61929 |
| C | 0.48823 | 2.02604 | 0.12417 |
| C | -0.17065 | 0.82197 | -0.13440 |
| C | -1.54035 | 0.77040 | 0.12501 |
| C | -2.24063 | 1.86417 | 0.62054 |
| C | -1.56008 | 3.05215 | 0.86780 |
| H | 0.34214 | 4.05208 | 0.81267 |
| H | 1.55519 | 2.08559 | -0.06185 |
| H | -3.30395 | 1.79408 | 0.81225 |
| H | -2.10092 | 3.90756 | 1.25428 |
| C | 0.57985 | -0.38393 | -0.66900 |
| H | 0.45527 | -1.22759 | 0.01110 |
| H | 0.15768 | -0.67123 | -1.63589 |
| N | 1.99662 | -0.15003 | -0.85390 |
| C | 3.03294 | -0.41830 | 0.02340 |
| C | 2.50025 | 0.40213 | -2.00579 |
| C | 4.20111 | -0.03457 | -0.61027 |
| C | 3.86647 | 0.49223 | -1.88521 |
| H | 1.83713 | 0.67086 | -2.81415 |
| H | 5.18521 | -0.13959 | -0.18118 |
| H | 4.54178 | 0.88030 | -2.63237 |
| C | 2.94054 | -1.03489 | 1.39655 |
| C | 1.83748 | -0.79698 | 2.18125 |
| H | 1.03721 | -0.13556 | 1.88257 |
| H | 1.79595 | -1.22761 | 3.17605 |
| O | 3.96816 | -1.72501 | 1.73723 |
| I | -2.63528 | -1.02805 | -0.23517 |

**Prod:** Triplet **S23** in DMSO
27
-643.3070148

| | | | |
|---|---|---|---|
| C | 2.42454 | 3.05870 | 0.83435 |
| C | 2.28273 | 1.82170 | 0.20566 |
| C | 1.09848 | 1.50018 | -0.46580 |
| C | 0.11395 | 2.46484 | -0.45441 |
| C | 0.19652 | 3.69455 | 0.14834 |
| C | 1.39428 | 3.99435 | 0.80913 |
| H | 3.34805 | 3.29000 | 1.35130 |
| H | 3.08975 | 1.09637 | 0.24306 |
| H | -0.62220 | 4.40440 | 0.12339 |
| H | 1.51234 | 4.95172 | 1.30327 |
| C | 0.86947 | 0.17649 | -1.16622 |
| H | -0.13084 | -0.19307 | -0.93372 |
| H | 0.91288 | 0.32288 | -2.24735 |
| N | 1.85465 | -0.83846 | -0.82632 |
| C | 1.81153 | -1.76805 | 0.19707 |
| C | 2.99442 | -1.03203 | -1.54831 |
| C | 2.95086 | -2.55063 | 0.09671 |
| C | 3.70442 | -2.07991 | -0.99891 |
| H | 3.20115 | -0.41299 | -2.40814 |
| H | 3.19419 | -3.36141 | 0.76529 |
| H | 4.64872 | -2.45882 | -1.35611 |
| C | 0.77051 | -1.92585 | 1.23569 |
| C | -0.03840 | -0.82219 | 1.67093 |
| H | 0.11150 | 0.19425 | 1.34130 |
| H | -0.77012 | -1.01916 | 2.44174 |
| O | 0.65136 | -3.02987 | 1.78868 |
| I | -3.02129 | -0.29998 | -0.23650 |




21 S23

**SM:** Singlet **21** in Benzene

27

-643.3105041

| | | | |
|---|---|---|---|
| C | -0.18927 | 3.12100 | 0.58735 |
| C | 0.49230 | 1.99629 | 0.14022 |
| C | -0.17445 | 0.79333 | -0.10569 |
| C | -1.54954 | 0.76710 | 0.12079 |
| C | -2.25060 | 1.88075 | 0.56826 |
| C | -1.56227 | 3.06648 | 0.80074 |
| H | 0.35526 | 4.03859 | 0.77510 |
| H | 1.56565 | 2.03159 | -0.01283 |
| H | -3.31885 | 1.82497 | 0.73552 |
| H | -2.10197 | 3.93845 | 1.15088 |
| C | 0.58125 | -0.43302 | -0.58425 |
| H | 0.50250 | -1.22551 | 0.16299 |
| H | 0.12667 | -0.79352 | -1.51161 |
| N | 1.98102 | -0.18229 | -0.83945 |
| C | 3.05754 | -0.40393 | 0.00198 |
| C | 2.42373 | 0.34838 | -2.02815 |
| C | 4.18879 | -0.01507 | -0.68964 |
| C | 3.79149 | 0.46851 | -1.96399 |
| H | 1.72174 | 0.57987 | -2.81500 |
| H | 5.18798 | -0.09880 | -0.29290 |
| H | 4.42795 | 0.84543 | -2.75009 |
| C | 3.03648 | -0.99100 | 1.39692 |
| C | 1.96210 | -0.72292 | 2.21838 |
| H | 1.16782 | -0.04471 | 1.94020 |
| H | 1.96845 | -1.11297 | 3.22993 |
| O | 4.07214 | -1.66778 | 1.69508 |
| I | -2.65835 | -1.03058 | -0.20895 |

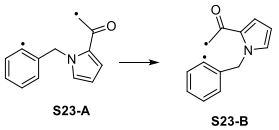
**Prod:** Triplet **S23** in Benzene

27

-643.2687235

| | | | |
|---|---|---|---|
| C | 1.16950 | 3.39675 | 0.96605 |
| C | 1.49399 | 2.21879 | 0.29350 |
| C | 0.51780 | 1.52400 | -0.42800 |
| C | -0.75127 | 2.06461 | -0.42530 |
| C | -1.12255 | 3.21392 | 0.22743 |
| C | -0.12885 | 3.89809 | 0.93617 |
| H | 1.93723 | 3.91958 | 1.52432 |
| H | 2.50661 | 1.82870 | 0.33847 |
| H | -2.14585 | 3.57132 | 0.20720 |
| H | -0.37480 | 4.80916 | 1.47031 |
| C | 0.79712 | 0.23558 | -1.17405 |
| H | 0.00713 | -0.48841 | -0.96209 |
| H | 0.77184 | 0.42170 | -2.24994 |
| N | 2.09867 | -0.33602 | -0.86314 |
| C | 2.42866 | -1.21794 | 0.14759 |
| C | 3.22520 | -0.03229 | -1.56775 |
| C | 3.78735 | -1.46826 | 0.05576 |
| C | 4.29489 | -0.71168 | -1.02191 |
| H | 3.16950 | 0.63931 | -2.41090 |
| H | 4.32589 | -2.13246 | 0.71290 |
| H | 5.31414 | -0.67026 | -1.37181 |
| C | 1.52467 | -1.82127 | 1.15748 |
| C | 0.31158 | -1.17485 | 1.57164 |
| H | 0.03914 | -0.16864 | 1.29267 |
| H | -0.31597 | -1.70551 | 2.27409 |
| O | 1.87706 | -2.87869 | 1.69687 |
| I | -2.83454 | -0.85652 | -0.24132 |

## 4.2 Radical Recombination



S23-A S23-B

**SM S23-A in DMSO**

26

-631.7419276

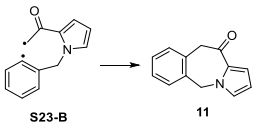
| | | | |
|---|---|---|---|
| C | 2.63794 | -0.35321 | 1.49596 |
| C | 1.44942 | -0.50963 | 0.78324 |
| C | 1.39954 | -0.21781 | -0.58419 |
| C | 2.57647 | 0.22132 | -1.15098 |
| C | 3.77193 | 0.39365 | -0.50229 |
| C | 3.79484 | 0.09465 | 0.86587 |
| H | 2.65614 | -0.58261 | 2.55458 |
| H | 0.55314 | -0.85447 | 1.29044 |
| H | 4.66066 | 0.74444 | -1.01418 |
| H | 4.71390 | 0.21431 | 1.42768 |
| C | 0.14046 | -0.35826 | -1.41807 |
| H | -0.07040 | 0.57031 | -1.95145 |
| H | 0.28810 | -1.12866 | -2.17665 |
| N | -1.02330 | -0.73812 | -0.63367 |
| C | -1.92889 | 0.07468 | 0.02671 |
| C | -1.36750 | -2.03939 | -0.42277 |
| C | -2.85348 | -0.75100 | 0.64668 |
| C | -2.49392 | -2.08603 | 0.37302 |
| H | -0.78581 | -2.83204 | -0.86872 |
| H | -3.68540 | -0.39946 | 1.23658 |
| H | -2.99570 | -2.98108 | 0.70418 |
| C | -1.94755 | 1.54934 | 0.08499 |
| C | -0.75294 | 2.33544 | -0.08943 |
| H | 0.23908 | 1.91207 | -0.14312 |
| H | -0.86723 | 3.41120 | -0.08715 |
| O | -3.01266 | 2.12131 | 0.35139 |

**S23-B** in DMSO in conformation for $S_{RN}1$ cyclisation

26

-631.7389322

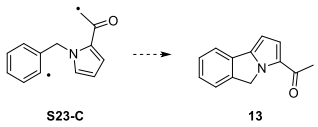
| | | | |
|---|---|---|---|
| C | -3.47356 | -0.93170 | -0.39313 |
| C | -2.26951 | -1.12262 | 0.27746 |
| C | -1.45112 | -0.03136 | 0.60469 |
| C | -1.93545 | 1.20339 | 0.24110 |
| C | -3.11377 | 1.45834 | -0.41771 |
| C | -3.89913 | 0.34919 | -0.74330 |
| H | -4.08972 | -1.78843 | -0.63769 |
| H | -1.96586 | -2.12517 | 0.56101 |
| H | -3.42576 | 2.46382 | -0.67459 |
| H | -4.84052 | 0.48926 | -1.26183 |
| C | -0.13488 | -0.21899 | 1.33272 |
| H | 0.20276 | 0.71604 | 1.77539 |
| H | -0.26873 | -0.93384 | 2.14591 |
| N | 0.92708 | -0.74540 | 0.47005 |
| C | 1.99612 | -0.07831 | -0.10508 |
| C | 1.04623 | -2.07459 | 0.19302 |
| C | 2.78013 | -1.02132 | -0.75043 |
| C | 2.17504 | -2.28107 | -0.57304 |
| H | 0.33403 | -2.78197 | 0.58885 |
| H | 3.68144 | -0.79076 | -1.29639 |
| H | 2.51913 | -3.23286 | -0.94544 |
| C | 2.30239 | 1.36468 | -0.06518 |
| C | 1.27096 | 2.35914 | 0.07191 |
| H | 0.21526 | 2.12864 | 0.03027 |
| H | 1.58218 | 3.39302 | 0.14097 |
| O | 3.47569 | 1.72893 | -0.21938 |



S23-B 11

**Product 11** in DMSO
26
-631.7856371

| | | | |
|---|---|---|---|
| C | -3.23615 | -1.12117 | -0.67279 |
| C | -2.09499 | -1.59048 | -0.02810 |
| C | -1.15827 | -0.70098 | 0.49233 |
| C | -1.35577 | 0.68255 | 0.36496 |
| C | -2.49832 | 1.14099 | -0.28951 |
| C | -3.43592 | 0.24868 | -0.80370 |
| H | -3.96141 | -1.82149 | -1.06974 |
| H | -1.93038 | -2.65803 | 0.07443 |
| H | -2.65768 | 2.20917 | -0.39218 |
| H | -4.32099 | 0.62525 | -1.30297 |
| C | 0.08912 | -1.20899 | 1.17255 |
| H | 0.19255 | -0.78663 | 2.17698 |
| H | 0.05270 | -2.29280 | 1.27360 |
| N | 1.28654 | -0.88838 | 0.39764 |
| C | 1.66300 | 0.35259 | -0.03596 |
| C | 2.24301 | -1.83320 | -0.03459 |
| C | 2.94172 | 0.16858 | -0.78111 |
| C | 3.24731 | -1.16696 | -0.75292 |
| H | 2.12097 | -2.87836 | 0.20123 |
| H | 3.47684 | 0.97999 | -1.24505 |
| H | 4.10198 | -1.65136 | -1.19835 |
| C | 0.99843 | 1.58374 | 0.16748 |
| C | -0.33150 | 1.65203 | 0.90782 |
| H | -0.69490 | 2.67410 | 0.79989 |
| H | -0.17849 | 1.47868 | 1.97980 |
| O | 1.54538 | 2.63698 | -0.28999 |



S23-C 13

**SM S23-C** in DMSO
26
-631.7377405

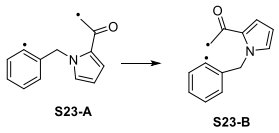
| | | | |
|---|---|---|---|
| C | 3.29759 | -1.32007 | -0.38802 |
| C | 2.03205 | -1.25568 | 0.19333 |
| C | 1.46931 | -0.02281 | 0.54411 |
| C | 2.26643 | 1.08082 | 0.32630 |
| C | 3.51284 | 1.08348 | -0.24533 |
| C | 4.03521 | -0.16188 | -0.61463 |
| H | 3.71267 | -2.28412 | -0.65555 |
| H | 1.49061 | -2.17308 | 0.40128 |
| H | 4.07619 | 1.99650 | -0.39869 |
| H | 5.01870 | -0.22096 | -1.06645 |
| C | 0.12653 | 0.09997 | 1.23012 |
| H | -0.21995 | -0.87849 | 1.56123 |
| H | 0.22056 | 0.73097 | 2.11485 |
| N | -0.90624 | 0.69410 | 0.36977 |
| C | -2.09268 | 0.13322 | -0.06628 |
| C | -0.94687 | 2.03619 | 0.12273 |
| C | -2.86915 | 1.14366 | -0.60463 |
| C | -2.13859 | 2.34740 | -0.49687 |
| H | -0.13293 | 2.67124 | 0.44020 |
| H | -3.83577 | 0.99549 | -1.06122 |
| H | -2.44123 | 3.32790 | -0.82834 |
| C | -2.42586 | -1.30296 | -0.07703 |
| C | -1.38607 | -2.26264 | -0.34339 |
| H | -0.41125 | -1.94906 | -0.68838 |
| H | -1.62526 | -3.31647 | -0.29242 |
| O | -3.59913 | -1.66884 | 0.05033 |

**TS S23-C** in DMSO
26
-631.7281116

| | | | |
|---|---|---|---|
| C | 3.36451 | -1.25743 | -0.49701 |
| C | 2.20395 | -1.59006 | 0.20146 |
| C | 1.28891 | -0.58978 | 0.52929 |
| C | 1.57324 | 0.70398 | 0.14036 |
| C | 2.70717 | 1.07445 | -0.54724 |
| C | 3.61772 | 0.06126 | -0.87104 |
| H | 4.07388 | -2.03450 | -0.75573 |
| H | 2.01245 | -2.62081 | 0.48387 |
| H | 2.89737 | 2.10270 | -0.83563 |
| H | 4.52161 | 0.30560 | -1.41805 |
| C | -0.00584 | -0.80582 | 1.28808 |
| H | -0.48310 | -1.74386 | 1.00946 |
| H | 0.16850 | -0.81903 | 2.36679 |
| N | -0.87310 | 0.33033 | 0.96269 |
| C | -1.75076 | 0.34934 | -0.11202 |
| C | -0.29222 | 1.58507 | 1.05036 |
| C | -1.81915 | 1.64317 | -0.60548 |
| C | -0.93338 | 2.43380 | 0.14277 |
| H | 0.30024 | 1.84514 | 1.91541 |
| H | -2.49012 | 1.96686 | -1.38630 |
| H | -0.76606 | 3.49545 | 0.05202 |
| C | -2.59248 | -0.78315 | -0.52837 |
| C | -2.93385 | -1.81134 | 0.42176 |
| H | -2.69672 | -1.72267 | 1.47298 |
| H | -3.50264 | -2.66204 | 0.07162 |
| O | -3.06132 | -0.81325 | -1.67409 |

**Prod 13** cyclisation in DMSO
XYZ_Diradical_RadicalRecom_Prod.log
26
-631.7863794

| | | | |
|---|---|---|---|
| C | 3.55933 | -1.03398 | -0.64531 |
| C | 2.35228 | -1.65443 | -0.32719 |
| C | 1.31253 | -0.87514 | 0.16359 |
| C | 1.47603 | 0.49478 | 0.33945 |
| C | 2.67690 | 1.11855 | 0.02907 |
| C | 3.72037 | 0.34090 | -0.46945 |
| H | 4.37996 | -1.62453 | -1.03511 |
| H | 2.22881 | -2.72281 | -0.46571 |
| H | 2.80231 | 2.18689 | 0.16744 |
| H | 4.66436 | 0.80813 | -0.72374 |
| C | -0.07582 | -1.30121 | 0.57955 |
| H | -0.58101 | -1.87619 | -0.19874 |
| H | -0.05531 | -1.90020 | 1.49435 |
| N | -0.77018 | -0.01490 | 0.80877 |
| C | -1.81108 | 0.39039 | -0.01260 |
| C | 0.20591 | 1.10081 | 0.89605 |
| C | -1.61196 | 1.74914 | -0.40959 |
| C | -0.44455 | 2.19966 | 0.10249 |
| H | 0.35804 | 1.40411 | 1.94076 |
| H | -2.32137 | 2.30471 | -1.00540 |
| H | -0.02888 | 3.19319 | 0.01617 |
| C | -2.97313 | -0.41545 | -0.30525 |
| C | -3.21451 | -1.65576 | 0.40361 |
| H | -2.61569 | -1.96190 | 1.25024 |
| H | -4.05595 | -2.26073 | 0.09633 |
| O | -3.80223 | -0.02449 | -1.15807 |

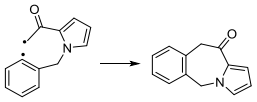



**SM S23-A** in Benzene
26
-631.7362148

| | | | |
|---|---|---|---|
| C | 2.63201 | -0.35421 | 1.49600 |
| C | 1.44510 | -0.51108 | 0.78155 |
| C | 1.39852 | -0.21908 | -0.58580 |
| C | 2.57577 | 0.22065 | -1.15065 |
| C | 3.76964 | 0.39321 | -0.49945 |
| C | 3.78969 | 0.09408 | 0.86818 |
| H | 2.64832 | -0.58327 | 2.55467 |
| H | 0.54644 | -0.85512 | 1.28519 |
| H | 4.65887 | 0.74435 | -1.01005 |
| H | 4.70743 | 0.21394 | 1.43211 |
| C | 0.13881 | -0.35863 | -1.41931 |
| H | -0.07104 | 0.57208 | -1.94992 |
| H | 0.28786 | -1.12697 | -2.18029 |
| N | -1.02420 | -0.73909 | -0.63795 |
| C | -1.92570 | 0.07387 | 0.02796 |
| C | -1.36876 | -2.04154 | -0.42478 |
| C | -2.84720 | -0.74962 | 0.65099 |
| C | -2.49047 | -2.08580 | 0.37538 |
| H | -0.78929 | -2.83467 | -0.87251 |
| H | -3.67803 | -0.39304 | 1.23897 |
| H | -2.99385 | -2.97959 | 0.70698 |
| C | -1.94560 | 1.55115 | 0.08442 |
| C | -0.75022 | 2.33864 | -0.09344 |
| H | 0.24407 | 1.91843 | -0.13588 |
| H | -0.87109 | 3.41368 | -0.09305 |
| O | -3.00622 | 2.12175 | 0.35289 |

**S23-B** in DMSO in conformation for $S_{RN}1$ cyclisation
26
-631.7324459

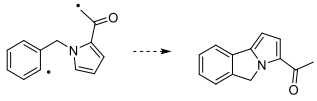
| | | | |
|---|---|---|---|
| C | -3.50592 | -0.91638 | -0.34556 |
| C | -2.29777 | -1.10732 | 0.31684 |
| C | -1.45611 | -0.02245 | 0.60032 |
| C | -1.92149 | 1.20852 | 0.20164 |
| C | -3.10263 | 1.46345 | -0.45132 |
| C | -3.91193 | 0.35994 | -0.73170 |
| H | -4.14009 | -1.76872 | -0.55687 |
| H | -2.00641 | -2.10598 | 0.62619 |
| H | -3.39899 | 2.46583 | -0.73690 |
| H | -4.85661 | 0.50057 | -1.24405 |
| C | -0.13352 | -0.21236 | 1.31596 |
| H | 0.20995 | 0.72499 | 1.74980 |
| H | -0.26475 | -0.92115 | 2.13567 |
| N | 0.91950 | -0.74453 | 0.44968 |
| C | 2.00669 | -0.08881 | -0.10397 |
| C | 1.02420 | -2.07428 | 0.16222 |
| C | 2.78595 | -1.03541 | -0.74493 |
| C | 2.16051 | -2.28872 | -0.58759 |
| H | 0.29623 | -2.77437 | 0.54153 |
| H | 3.69909 | -0.80964 | -1.27237 |
| H | 2.49783 | -3.24137 | -0.96343 |
| C | 2.32766 | 1.35265 | -0.05121 |
| C | 1.29783 | 2.35500 | 0.05855 |
| H | 0.24239 | 2.13210 | -0.02275 |
| H | 1.61781 | 3.38550 | 0.13720 |
| O | 3.50327 | 1.70764 | -0.17217 |



S23-B 11

**Product 11** in Benzene
26
-631.7777499

| | | | |
|---|---|---|---|
| C | -3.24319 | -1.11523 | -0.66482 |
| C | -2.10426 | -1.58419 | -0.01737 |
| C | -1.16297 | -0.69582 | 0.49588 |
| C | -1.35329 | 0.68781 | 0.35930 |
| C | -2.49345 | 1.14503 | -0.29943 |
| C | -3.43517 | 0.25410 | -0.80658 |
| H | -3.97183 | -1.81483 | -1.05663 |
| H | -1.94499 | -2.65205 | 0.09228 |
| H | -2.64551 | 2.21302 | -0.41292 |
| H | -4.31750 | 0.63140 | -1.30995 |
| C | 0.08497 | -1.20577 | 1.17377 |
| H | 0.19163 | -0.77835 | 2.17675 |
| H | 0.04131 | -2.28937 | 1.28189 |
| N | 1.28021 | -0.89748 | 0.39577 |
| C | 1.66408 | 0.34953 | -0.03524 |
| C | 2.23195 | -1.84146 | -0.04028 |
| C | 2.94475 | 0.16117 | -0.77791 |
| C | 3.24202 | -1.17437 | -0.75484 |
| H | 2.10392 | -2.88857 | 0.18322 |
| H | 3.47952 | 0.97590 | -1.23635 |
| H | 4.09443 | -1.66077 | -1.20257 |
| C | 1.00926 | 1.58183 | 0.16793 |
| C | -0.32849 | 1.65935 | 0.89643 |
| H | -0.68363 | 2.68225 | 0.77179 |
| H | -0.18340 | 1.50086 | 1.97188 |
| O | 1.56717 | 2.62886 | -0.27634 |



S23-C 13

**SM S23-C** in Benzene
26
-631.7348295

| | | | |
|---|---|---|---|
| C | -3.51878 | 0.98611 | 0.05748 |
| C | -2.31151 | 0.97903 | 0.75302 |
| C | -1.40716 | -0.07737 | 0.59670 |
| C | -1.79356 | -1.08320 | -0.26102 |
| C | -2.96371 | -1.12737 | -0.97553 |
| C | -3.84770 | -0.05675 | -0.80447 |
| H | -4.20478 | 1.81450 | 0.18566 |
| H | -2.06237 | 1.80139 | 1.41782 |
| H | -3.20024 | -1.94958 | -1.64073 |
| H | -4.78606 | -0.04116 | -1.34655 |
| C | -0.10867 | -0.14370 | 1.37192 |
| H | 0.16326 | 0.84225 | 1.75059 |
| H | -0.23425 | -0.79584 | 2.23928 |
| N | 0.99722 | -0.67771 | 0.58720 |
| C | 1.99529 | 0.00758 | -0.08169 |
| C | 1.24268 | -2.01572 | 0.48443 |
| C | 2.87173 | -0.92812 | -0.60127 |
| C | 2.39010 | -2.20788 | -0.25564 |
| H | 0.58749 | -2.72535 | 0.96655 |
| H | 3.74779 | -0.68188 | -1.18049 |
| H | 2.82666 | -3.16111 | -0.50656 |
| C | 2.10581 | 1.46904 | -0.25777 |
| C | 0.92269 | 2.29159 | -0.32802 |
| H | -0.07120 | 1.87596 | -0.41851 |
| H | 1.06253 | 3.36254 | -0.39287 |
| O | 3.21591 | 1.98037 | -0.42166 |

**TS S23-C** in Benzene

26

-631.7173855

| | | | |
|---|---|---|---|
| C | 3.35734 | -1.12035 | -0.33860 |
| C | 2.26878 | -1.36982 | 0.49759 |
| C | 1.29950 | -0.38321 | 0.66794 |
| C | 1.45039 | 0.81972 | 0.00041 |
| C | 2.51691 | 1.10171 | -0.82387 |
| C | 3.48256 | 0.10163 | -0.99532 |
| H | 4.11021 | -1.88649 | -0.48133 |
| H | 2.17720 | -2.32480 | 1.00688 |
| H | 2.61385 | 2.05440 | -1.33324 |
| H | 4.33077 | 0.28042 | -1.64701 |
| C | 0.05665 | -0.48911 | 1.53458 |
| H | -0.37348 | -1.48776 | 1.57577 |
| H | 0.27484 | -0.18362 | 2.56164 |
| N | -0.88457 | 0.46666 | 0.96712 |
| C | -1.83606 | 0.24157 | -0.00604 |
| C | -0.40954 | 1.75926 | 0.81184 |
| C | -2.09389 | 1.44381 | -0.65309 |
| C | -1.21145 | 2.40292 | -0.14162 |
| H | 0.17179 | 2.21150 | 1.60257 |
| H | -2.84041 | 1.57239 | -1.42142 |
| H | -1.14590 | 3.44443 | -0.41350 |
| C | -2.44965 | -1.05662 | -0.36688 |
| C | -1.64881 | -2.25262 | -0.44605 |
| H | -0.56728 | -2.21975 | -0.45309 |
| H | -2.15792 | -3.19067 | -0.62271 |
| O | -3.63727 | -1.09125 | -0.69872 |

**Prod 13** cylisation in Benzene

26

-631.7808325

| | | | |
|---|---|---|---|
| C | 3.56443 | -1.03261 | -0.64193 |
| C | 2.35577 | -1.65236 | -0.33105 |
| C | 1.31482 | -0.87448 | 0.15846 |
| C | 1.47828 | 0.49413 | 0.34034 |
| C | 2.68102 | 1.11683 | 0.03676 |
| C | 3.72573 | 0.34087 | -0.46023 |
| H | 4.38581 | -1.62230 | -1.03122 |
| H | 2.23216 | -2.72002 | -0.47550 |
| H | 2.80693 | 2.18476 | 0.17801 |
| H | 4.67086 | 0.80832 | -0.70956 |
| C | -0.07629 | -1.29975 | 0.56570 |
| H | -0.58200 | -1.86268 | -0.22157 |
| H | -0.05936 | -1.91199 | 1.47247 |
| N | -0.76923 | -0.01668 | 0.80977 |
| C | -1.81343 | 0.38981 | -0.01064 |
| C | 0.20645 | 1.09960 | 0.89300 |
| C | -1.61320 | 1.74412 | -0.41373 |
| C | -0.44443 | 2.19601 | 0.09492 |
| H | 0.35688 | 1.40626 | 1.93735 |
| H | -2.32483 | 2.29284 | -1.01299 |
| H | -0.02794 | 3.18853 | 0.00179 |
| C | -2.97918 | -0.41408 | -0.30125 |
| C | -3.22169 | -1.65171 | 0.40976 |
| H | -2.62265 | -1.95719 | 1.25673 |
| H | -4.07179 | -2.24782 | 0.10929 |
| O | -3.80614 | -0.02252 | -1.15173 |

### 4.3 The isolated HOMO-LUMO fragments of 21


S24 S26

**SM (Before SET): S24** in DMSO

15

-282.2764280

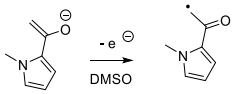
| | | | |
|---|---|---|---|
| C | -3.28995 | -0.39200 | 0.00000 |
| C | -2.66576 | 0.84989 | 0.00001 |
| C | -1.27245 | 0.97831 | -0.00000 |
| C | -0.53375 | -0.20839 | -0.00000 |
| C | -1.13558 | -1.46161 | 0.00000 |
| C | -2.52387 | -1.55233 | -0.00001 |
| H | -4.37155 | -0.45173 | -0.00000 |
| H | -3.26701 | 1.75271 | 0.00001 |
| H | -0.53158 | -2.36020 | -0.00001 |
| H | -2.99575 | -2.52737 | -0.00001 |
| I | 1.60244 | -0.14758 | 0.00000 |
| C | -0.63745 | 2.34153 | -0.00001 |
| H | -0.00416 | 2.47910 | 0.88028 |
| H | -0.00411 | 2.47908 | -0.88025 |
| H | -1.40259 | 3.11769 | -0.00004 |

**Prod (After SET): S26** in DMSO

15

-282.3841184

| | | | |
|---|---|---|---|
| C | -4.22541 | -0.38262 | -0.00069 |
| C | -3.56934 | 0.84888 | -0.00053 |
| C | -2.17036 | 0.92532 | 0.00026 |
| C | -1.51482 | -0.29045 | 0.00084 |
| C | -2.10314 | -1.53077 | 0.00071 |
| C | -3.50315 | -1.57234 | -0.00008 |
| H | -5.30871 | -0.40983 | -0.00131 |
| H | -4.14749 | 1.76788 | -0.00101 |
| H | -1.51653 | -2.44281 | 0.00120 |
| H | -4.01711 | -2.52674 | -0.00021 |
| I | 2.44999 | -0.10471 | -0.00011 |
| C | -1.43599 | 2.24108 | 0.00046 |
| H | -0.79503 | 2.32525 | 0.88067 |
| H | -0.79421 | 2.32506 | -0.87918 |
| H | -2.13704 | 3.07612 | 0.00004 |




S25 S27

**SM (Before SET): S25** in DMSO

17

-401.5715769

| | | | |
|---|---|---|---|
| C | 2.10188 | 0.14788 | 0.04160 |
| C | 2.02545 | -1.21550 | -0.13998 |
| C | 0.64382 | -1.54373 | -0.19784 |
| C | -0.07791 | -0.37121 | -0.05237 |
| N | 0.82936 | 0.65230 | 0.08578 |
| H | 2.95312 | 0.80234 | 0.14949 |
| H | 2.86375 | -1.88998 | -0.22522 |
| H | 0.20974 | -2.52117 | -0.34576 |
| C | 0.51909 | 2.05496 | 0.32219 |
| H | 0.14766 | 2.52866 | -0.58430 |
| H | -0.24430 | 2.14286 | 1.09449 |
| H | 1.42931 | 2.55117 | 0.65715 |
| C | -1.56107 | -0.12756 | -0.07978 |
| C | -2.34576 | -1.05328 | 0.56415 |
| H | -3.42676 | -0.96719 | 0.52981 |
| H | -1.90501 | -1.88126 | 1.10360 |
| O | -1.95825 | 0.91488 | -0.71594 |

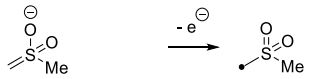
**Prod (After SET): S27** in DMSO

17

-401.4123853

| | | | |
|---|---|---|---|
| C | -2.09389 | 0.18436 | -0.03158 |
| C | -2.03252 | -1.19257 | -0.13543 |
| C | -0.66827 | -1.54042 | -0.10500 |
| C | 0.06404 | -0.36685 | -0.00122 |
| N | -0.83168 | 0.68517 | 0.04159 |
| H | -2.94407 | 0.84749 | 0.01315 |
| H | -2.87735 | -1.85754 | -0.21795 |
| H | -0.23530 | -2.52639 | -0.17136 |
| C | -0.55281 | 2.10277 | 0.24566 |
| H | 0.25372 | 2.22749 | 0.96677 |
| H | -0.28912 | 2.59255 | -0.69225 |
| H | -1.45133 | 2.56952 | 0.64365 |
| C | 1.53376 | -0.28221 | 0.02306 |
| C | 2.21796 | 0.90331 | -0.42801 |
| H | 3.29556 | 0.92481 | -0.33586 |
| H | 1.71452 | 1.72468 | -0.91434 |
| O | 2.19318 | -1.26864 | 0.37652 |

## 5. DMSO Possible Formation




S54 S55

**S55**

9

-552.6394561

| | | | |
|---|---|---|---|
| S | 0.11620 | 0.14532 | -0.41122 |
| C | 1.37804 | -0.82514 | 0.19707 |
| H | 2.33634 | -0.46410 | -0.17547 |
| H | 1.34642 | -0.92997 | 1.28568 |
| C | -1.31527 | -0.82293 | 0.13069 |
| H | -1.21349 | -0.99446 | 1.20441 |
| H | -2.21398 | -0.24264 | -0.07344 |
| H | -1.34041 | -1.76910 | -0.40571 |
| O | -0.14384 | 1.49544 | 0.34718 |

**S54**

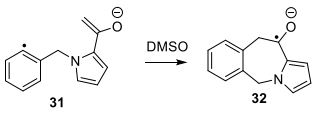
9

-552.4905292

| | | | |
|---|---|---|---|
| S | -0.10845 | -0.14067 | -0.41933 |
| C | -0.99298 | 1.21313 | 0.23115 |
| H | -0.66455 | 2.20876 | -0.03750 |
| H | -2.01291 | 1.01551 | 0.53267 |
| C | 1.53727 | 0.29296 | 0.20630 |
| H | 1.49395 | 0.31959 | 1.29417 |
| H | 2.21611 | -0.48349 | -0.14191 |
| H | 1.82330 | 1.26022 | -0.20606 |
| O | -0.54830 | -1.38830 | 0.33040 |

## 6. Radical Cyclisation of 9

### 6.1 DMSO (Scheme S2.1)

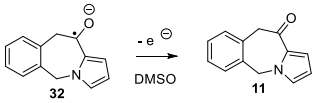



**SM: 31** cyclisation to **32** in DMSO
26
-631.9004297

| | | | |
|---|---|---|---|
| C | -2.73321 | -0.24997 | 1.46881 |
| C | -1.51740 | -0.34745 | 0.79266 |
| C | -1.43908 | -0.06963 | -0.57663 |
| C | -2.62254 | 0.29578 | -1.18084 |
| C | -3.84593 | 0.40838 | -0.57080 |
| C | -3.89495 | 0.12471 | 0.79976 |
| H | -2.77073 | -0.46932 | 2.52926 |
| H | -0.61652 | -0.63782 | 1.32527 |
| H | -4.73703 | 0.70032 | -1.11485 |
| H | -4.83619 | 0.19696 | 1.33251 |
| C | -0.14614 | -0.14734 | -1.36586 |
| H | -0.29852 | -0.78439 | -2.24021 |
| H | 0.13102 | 0.84661 | -1.71700 |
| N | 0.95989 | -0.68853 | -0.59962 |
| C | 1.13717 | -2.03963 | -0.43162 |
| C | 1.97371 | -0.00531 | 0.04656 |
| C | 2.26998 | -2.24094 | 0.32095 |
| H | 0.44438 | -2.73840 | -0.87608 |
| C | 2.80228 | -0.95738 | 0.61235 |
| H | 3.69321 | -0.72842 | 1.17614 |
| H | 2.66920 | -3.19919 | 0.61627 |
| C | 2.16332 | 1.48827 | 0.12080 |
| C | 1.06007 | 2.29996 | 0.22510 |
| H | 0.05565 | 1.90693 | 0.29775 |
| H | 1.19697 | 3.37341 | 0.30032 |
| O | 3.38819 | 1.87454 | 0.12507 |

**Prod: 32** cyclised in DMSO
26
-631.9716451

| | | | |
|---|---|---|---|
| C | 3.20248 | -1.13436 | -0.66836 |
| C | 2.07161 | -1.58973 | 0.00598 |
| C | 1.14374 | -0.69065 | 0.52606 |
| C | 1.33639 | 0.69138 | 0.36891 |
| C | 2.46994 | 1.13552 | -0.31364 |
| C | 3.39892 | 0.23380 | -0.82882 |
| H | 3.92186 | -1.84193 | -1.06397 |
| H | 1.90747 | -2.65555 | 0.13099 |
| H | 2.62842 | 2.20195 | -0.43921 |
| H | 4.27569 | 0.60051 | -1.35047 |
| C | -0.11209 | -1.17057 | 1.20902 |
| H | -0.07093 | -2.24938 | 1.36177 |
| H | -0.22159 | -0.70211 | 2.19351 |
| N | -1.28916 | -0.89095 | 0.40117 |
| C | -2.17400 | -1.86261 | -0.02910 |
| C | -1.69304 | 0.36422 | -0.06993 |
| C | -3.15891 | -1.25065 | -0.77192 |
| H | -2.02068 | -2.89684 | 0.23709 |
| C | -2.87789 | 0.13744 | -0.80685 |
| H | -3.44009 | 0.90587 | -1.31317 |
| H | -3.99182 | -1.75637 | -1.23877 |
| C | -1.02377 | 1.60374 | 0.15698 |
| C | 0.31089 | 1.65890 | 0.90611 |
| H | 0.17592 | 1.49319 | 1.98467 |
| H | 0.68336 | 2.67795 | 0.79193 |
| O | -1.52363 | 2.71259 | -0.27614 |



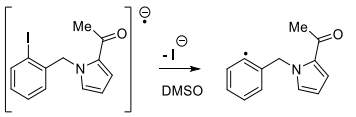

32 11

**Prod (After SET): 11** in DMSO

26

-631.8980850

| | | | |
|---|---|---|---|
| C | 3.22968 | -1.12300 | -0.66874 |
| C | 2.07908 | -1.60447 | -0.04937 |
| C | 1.13629 | -0.72203 | 0.46962 |
| C | 1.34190 | 0.65928 | 0.37190 |
| C | 2.49217 | 1.13391 | -0.25355 |
| C | 3.43476 | 0.24820 | -0.77096 |
| H | 3.95928 | -1.81671 | -1.06914 |
| H | 1.91189 | -2.67322 | 0.03168 |
| H | 2.65423 | 2.20354 | -0.33074 |
| H | 4.32737 | 0.63173 | -1.25073 |
| C | -0.11543 | -1.22897 | 1.13930 |
| H | -0.09034 | -2.31386 | 1.22672 |
| H | -0.21084 | -0.81551 | 2.14727 |
| N | -1.31780 | -0.89133 | 0.37382 |
| C | -2.23824 | -1.80310 | -0.02365 |
| C | -1.70667 | 0.36076 | -0.07345 |
| C | -3.23937 | -1.15891 | -0.73265 |
| H | -2.11417 | -2.84619 | 0.22367 |
| C | -2.90235 | 0.20413 | -0.76421 |
| H | -3.44805 | 1.00927 | -1.23105 |
| H | -4.10292 | -1.63170 | -1.17226 |
| C | -0.98781 | 1.61730 | 0.14334 |
| C | 0.31507 | 1.61627 | 0.92979 |
| H | 0.07974 | 1.35476 | 1.96833 |
| H | 0.69244 | 2.63778 | 0.92086 |
| O | -1.43356 | 2.66291 | -0.29821 |




33 34

**TS: 33** C-I elongation to give **34** in DMSO

28

-643.9223676

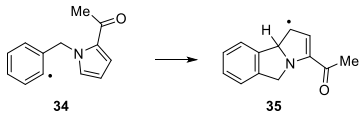
| | | | |
|---|---|---|---|
| C | 0.48610 | 3.05031 | 0.42108 |
| C | 0.93172 | 1.85744 | -0.13740 |
| C | 0.06284 | 0.77512 | -0.32724 |
| C | -1.24423 | 0.97526 | 0.07610 |
| C | -1.73502 | 2.14067 | 0.63405 |
| C | -0.84252 | 3.19639 | 0.80844 |
| H | 1.18216 | 3.86946 | 0.55573 |
| H | 1.97009 | 1.74459 | -0.43259 |
| H | -2.77201 | 2.23162 | 0.92729 |
| H | -1.19278 | 4.12390 | 1.24546 |
| C | 0.54580 | -0.51976 | -0.96062 |
| H | 0.10440 | -1.36254 | -0.43401 |
| H | 0.17271 | -0.56746 | -1.98791 |
| N | 1.98448 | -0.63619 | -1.00994 |
| C | 2.84452 | -0.63766 | 0.11086 |
| C | 2.68730 | -0.16627 | -2.11975 |
| C | 4.09930 | -0.18610 | -0.35838 |
| C | 3.98248 | 0.09000 | -1.74290 |
| H | 2.19062 | -0.07141 | -3.07317 |
| H | 4.98908 | -0.12089 | 0.24740 |
| H | 4.76884 | 0.42441 | -2.40439 |
| C | 2.51764 | -1.03020 | 1.43920 |
| C | 1.21051 | -1.72888 | 1.77244 |
| H | 0.34005 | -1.05893 | 1.78323 |
| H | 0.98295 | -2.54820 | 1.08137 |
| O | 3.37686 | -0.86603 | 2.38843 |
| I | -2.79681 | -0.75524 | -0.18895 |
| H | 1.30956 | -2.15286 | 2.77284 |

**Prod: 34** + Iodide anion in DMSO

28

-643.9665259

| | | | |
|---|---|---|---|
| C | 1.61061 | 3.28725 | 0.44105 |
| C | 1.75340 | 2.03697 | -0.15938 |
| C | 0.62506 | 1.28615 | -0.50875 |
| C | -0.60015 | 1.85200 | -0.22662 |
| C | -0.79512 | 3.07634 | 0.36547 |
| C | 0.34718 | 3.81050 | 0.70463 |
| H | 2.49453 | 3.85420 | 0.70800 |
| H | 2.74541 | 1.63763 | -0.35100 |
| H | -1.78794 | 3.46249 | 0.56816 |
| H | 0.24504 | 4.78188 | 1.17520 |
| C | 0.71973 | -0.07087 | -1.17583 |
| H | -0.08498 | -0.71316 | -0.82199 |
| H | 0.58542 | 0.03802 | -2.25394 |
| N | 2.02036 | -0.70250 | -0.98138 |
| C | 2.59246 | -1.15269 | 0.20008 |
| C | 2.97907 | -0.68168 | -1.94603 |
| C | 3.92543 | -1.43478 | -0.06557 |
| C | 4.17052 | -1.14312 | -1.41973 |
| H | 2.73951 | -0.32978 | -2.93794 |
| H | 4.61727 | -1.83654 | 0.65829 |
| H | 5.09643 | -1.26054 | -1.95958 |
| C | 1.93832 | -1.36633 | 1.50217 |
| C | 0.43726 | -1.34483 | 1.63081 |
| H | 0.03630 | -0.34848 | 1.42834 |
| H | -0.02447 | -2.03378 | 0.92000 |
| O | 2.63630 | -1.60308 | 2.47626 |
| I | -3.21306 | -0.69439 | -0.16554 |
| H | 0.17380 | -1.63667 | 2.64578 |




34 35

**SM: 34** cyclisation to **35** in DMSO

27

-632.4034071

| | | | |
|---|---|---|---|
| C | -2.25369 | -0.20247 | 1.70411 |
| C | -1.21388 | -0.46653 | 0.84509 |
| C | -1.28560 | -0.47851 | -0.52875 |
| C | -2.54046 | -0.19943 | -1.08451 |
| C | -3.63157 | 0.06905 | -0.26337 |
| C | -3.49602 | 0.07024 | 1.12447 |
| H | -2.12458 | -0.20319 | 2.78022 |
| H | -4.59502 | 0.28355 | -0.70984 |
| H | -4.34989 | 0.28617 | 1.75621 |
| C | -0.09207 | -0.77758 | -1.41044 |
| H | -0.21815 | -1.75321 | -1.88277 |
| H | -0.01683 | -0.04561 | -2.21401 |
| N | 1.15349 | -0.83631 | -0.65611 |
| C | 1.72816 | -2.02126 | -0.31429 |
| C | 1.77755 | 0.17835 | 0.05605 |
| C | 2.74824 | -1.79332 | 0.58858 |
| H | 1.35848 | -2.94360 | -0.73610 |
| C | 2.77384 | -0.40669 | 0.82457 |
| H | 3.45220 | 0.14315 | 1.45794 |
| H | 3.39692 | -2.54374 | 1.01124 |
| C | 1.51280 | 1.62506 | -0.00086 |
| C | 0.65557 | 2.21983 | -1.09078 |
| H | -0.38742 | 1.91795 | -0.96808 |
| H | 0.72046 | 3.30404 | -1.02382 |
| O | 2.03157 | 2.35060 | 0.83278 |
| H | -2.65589 | -0.18906 | -2.16420 |
| H | 0.99543 | 1.89255 | -2.07519 |

**TS: 34** cyclisation to **35** in DMSO

27

-632.3878362

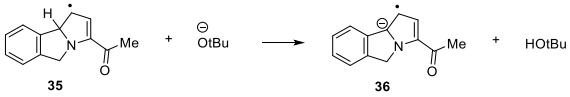
| | | | |
|---|---|---|---|
| C | -2.74967 | 1.07494 | -0.54232 |
| C | -1.61746 | 0.70058 | 0.14464 |
| C | -1.32200 | -0.59506 | 0.51610 |
| C | -2.22651 | -1.59766 | 0.16726 |
| C | -3.38554 | -1.26376 | -0.53338 |
| C | -3.64861 | 0.05837 | -0.88790 |
| H | -2.94691 | 2.10619 | -0.81436 |
| H | -4.08620 | -2.04272 | -0.80944 |
| H | -4.55098 | 0.30325 | -1.43708 |
| C | -0.02968 | -0.80909 | 1.28069 |
| H | -0.21149 | -0.81917 | 2.35831 |
| H | 0.45062 | -1.74459 | 1.01004 |
| N | 0.83291 | 0.33286 | 0.96354 |
| C | 0.24381 | 1.57775 | 1.07941 |
| C | 1.71916 | 0.38362 | -0.10557 |
| C | 0.87980 | 2.45738 | 0.19511 |
| H | -0.35865 | 1.81025 | 1.94561 |
| C | 1.77636 | 1.69653 | -0.56232 |
| H | 2.45290 | 2.04539 | -1.32730 |
| H | 0.70268 | 3.51942 | 0.13248 |
| C | 2.60285 | -0.69863 | -0.55389 |
| C | 2.85016 | -1.89756 | 0.33200 |
| H | 2.19547 | -2.71845 | 0.02596 |
| H | 3.87906 | -2.22193 | 0.18007 |
| O | 3.17941 | -0.59733 | -1.62623 |
| H | -2.02802 | -2.63088 | 0.43528 |
| H | 2.67989 | -1.68267 | 1.38644 |

**Prod: 35** in DMSO

27

-632.4493559

| | | | |
|---|---|---|---|
| C | -2.71868 | 1.11644 | 0.02551 |
| C | -1.51273 | 0.49955 | 0.32838 |
| C | -1.34430 | -0.87105 | 0.16069 |
| C | -2.38510 | -1.65833 | -0.31409 |
| C | -3.59750 | -1.04483 | -0.62559 |
| C | -3.76285 | 0.33051 | -0.45860 |
| H | -2.84779 | 2.18492 | 0.15862 |
| H | -4.41920 | -1.64168 | -1.00328 |
| H | -4.71102 | 0.79182 | -0.70792 |
| C | 0.05215 | -1.28849 | 0.56082 |
| H | 0.05061 | -1.88389 | 1.47785 |
| H | 0.55191 | -1.85898 | -0.22248 |
| N | 0.73547 | 0.00368 | 0.77148 |
| C | -0.24261 | 1.11058 | 0.87721 |
| C | 1.79415 | 0.42252 | -0.00631 |
| C | 0.40706 | 2.22384 | 0.10652 |
| H | -0.38711 | 1.40091 | 1.92724 |
| C | 1.58623 | 1.79857 | -0.38405 |
| H | 2.30336 | 2.36919 | -0.95532 |
| H | -0.01639 | 3.21531 | 0.03136 |
| C | 2.96123 | -0.35378 | -0.32023 |
| C | 3.16882 | -1.69687 | 0.34439 |
| H | 2.84032 | -2.50092 | -0.32009 |
| H | 4.23634 | -1.82837 | 0.52208 |
| O | 3.80584 | 0.08803 | -1.11463 |
| H | -2.25837 | -2.72711 | -0.44603 |
| H | 2.62704 | -1.78297 | 1.28659 |




**SM: 35** + tert-butoxide anion in DMSO

41

-865.5794437

| | | | |
|---|---|---|---|
| C | -0.56013 | 2.48129 | 0.96682 |
| C | 0.18440 | 1.51200 | 0.30678 |
| C | 1.21127 | 1.87118 | -0.56259 |
| C | 1.51636 | 3.20692 | -0.78786 |
| C | 0.77719 | 4.18370 | -0.12118 |
| C | -0.25134 | 3.82359 | 0.74961 |
| H | -1.36383 | 2.20286 | 1.63963 |
| H | 1.00524 | 5.23125 | -0.27907 |
| H | -0.81494 | 4.59465 | 1.26185 |
| C | 1.85861 | 0.64032 | -1.15687 |
| H | 1.65229 | 0.55135 | -2.22750 |
| H | 2.93990 | 0.63218 | -1.01235 |
| N | 1.22872 | -0.45901 | -0.40216 |
| C | 0.03174 | 0.01147 | 0.33506 |
| C | 1.93099 | -1.33750 | 0.39134 |
| C | 0.13455 | -0.70904 | 1.64244 |
| H | -0.90467 | -0.26952 | -0.21372 |
| C | 1.22592 | -1.49932 | 1.64089 |
| H | 1.54767 | -2.17729 | 2.41771 |
| H | -0.61375 | -0.63777 | 2.42011 |
| C | 3.11927 | -2.04367 | 0.01421 |
| C | 3.62013 | -1.95970 | -1.41180 |
| H | 4.40837 | -1.20591 | -1.49428 |
| H | 4.05396 | -2.92376 | -1.67866 |
| O | 3.72688 | -2.74239 | 0.84627 |
| H | 2.31670 | 3.48853 | -1.46328 |
| H | 2.82766 | -1.70885 | -2.11750 |
| O | -2.46892 | -0.56656 | -1.27368 |
| C | -3.43304 | -1.02483 | -0.40421 |
| C | -4.79051 | -1.20816 | -1.11624 |
| H | -4.68301 | -1.93016 | -1.93183 |
| H | -5.57561 | -1.56549 | -0.43983 |
| H | -5.11165 | -0.25377 | -1.54573 |
| C | -3.64443 | -0.03325 | 0.76429 |
| H | -2.70570 | 0.09760 | 1.31175 |
| H | -3.94428 | 0.94276 | 0.36910 |
| H | -4.40925 | -0.37153 | 1.47257 |
| C | -3.02469 | -2.38715 | 0.20158 |
| H | -2.90086 | -3.12173 | -0.60055 |
| H | -2.06452 | -2.28416 | 0.71793 |
| H | -3.76218 | -2.77375 | 0.91440 |

**TS: 35** + tert-butoxide anion in DMSO

41

-865.5785755

| | | | |
|---|---|---|---|
| C | -0.91934 | 2.39230 | 0.99531 |
| C | -0.03961 | 1.51988 | 0.36417 |
| C | 0.92844 | 2.00905 | -0.51540 |
| C | 1.03104 | 3.36687 | -0.78154 |
| C | 0.15310 | 4.24443 | -0.14451 |
| C | -0.81167 | 3.75896 | 0.73828 |
| H | -1.67458 | 2.01964 | 1.67829 |
| H | 0.22313 | 5.30897 | -0.33422 |
| H | -1.48552 | 4.45164 | 1.22934 |
| C | 1.76063 | 0.87430 | -1.07094 |
| H | 1.61285 | 0.75466 | -2.14907 |
| H | 2.82821 | 1.01297 | -0.88593 |
| N | 1.25808 | -0.28973 | -0.32682 |
| C | 0.02793 | 0.02477 | 0.41572 |
| C | 2.02922 | -1.16648 | 0.40310 |
| C | 0.19606 | -0.71963 | 1.68447 |
| H | -0.91268 | -0.41637 | -0.19747 |
| C | 1.34022 | -1.44091 | 1.64015 |
| H | 1.70448 | -2.14083 | 2.37817 |
| H | -0.54769 | -0.74157 | 2.46987 |
| C | 3.25571 | -1.76047 | -0.01880 |
| C | 3.74462 | -1.54311 | -1.43630 |
| H | 2.93363 | -1.31012 | -2.12700 |
| H | 4.47196 | -0.72667 | -1.47032 |
| O | 3.92458 | -2.47393 | 0.76081 |
| H | 1.78304 | 3.74341 | -1.46681 |
| O | -1.99867 | -0.93909 | -1.12285 |
| C | -3.11725 | -1.35790 | -0.41784 |
| C | -4.30825 | -1.55068 | -1.37299 |
| H | -4.05355 | -2.29124 | -2.13688 |
| H | -5.20807 | -1.88951 | -0.84786 |
| H | -4.53620 | -0.60574 | -1.87518 |
| C | -3.51679 | -0.31462 | 0.64634 |
| H | -2.70951 | -0.19027 | 1.37465 |
| H | -3.69172 | 0.65278 | 0.16569 |
| H | -4.42264 | -0.60335 | 1.18986 |
| C | -2.83888 | -2.69610 | 0.29579 |
| H | -2.57958 | -3.46007 | -0.44381 |
| H | -1.98978 | -2.57944 | 0.97679 |
| H | -3.70125 | -3.04919 | 0.87182 |
| H | 4.25041 | -2.45147 | -1.76584 |

**Prod: 36** + tert-butanol in DMSO
41
-865.6231594

| | | | |
|---|---|---|---|
| C | 2.82167 | -0.62636 | 1.29333 |
| C | 1.58573 | -0.95655 | 0.72539 |
| C | 1.53381 | -1.47941 | -0.58724 |
| C | 2.68826 | -1.68087 | -1.32011 |
| C | 3.92335 | -1.35190 | -0.74853 |
| C | 3.97814 | -0.82831 | 0.54667 |
| H | 2.87773 | -0.21718 | 2.29606 |
| H | 4.83734 | -1.50245 | -1.31011 |
| H | 4.94043 | -0.57563 | 0.97828 |
| C | 0.09404 | -1.72900 | -0.98764 |
| H | -0.22197 | -1.09386 | -1.82533 |
| H | -0.07130 | -2.77399 | -1.26671 |
| N | -0.62123 | -1.36368 | 0.23115 |
| C | 0.23900 | -0.84271 | 1.20313 |
| C | -1.94653 | -1.02438 | 0.53062 |
| C | -0.53663 | -0.21253 | 2.17067 |
| H | -0.82768 | 1.04344 | -0.04327 |
| C | -1.87708 | -0.32101 | 1.77039 |
| H | -2.74093 | 0.04755 | 2.30118 |
| H | -0.16267 | 0.28197 | 3.05563 |
| C | -3.11728 | -1.30433 | -0.21901 |
| C | -3.08842 | -2.16675 | -1.46386 |
| H | -3.84388 | -2.95313 | -1.36146 |
| H | -3.36334 | -1.57593 | -2.34501 |
| O | -4.25628 | -0.84909 | 0.15056 |
| H | 2.64058 | -2.08048 | -2.32801 |
| H | -2.13006 | -2.64452 | -1.65631 |
| O | -0.66352 | 1.58100 | -0.83054 |
| C | -0.05613 | 2.81164 | -0.41513 |
| C | 0.05607 | 3.65805 | -1.67556 |
| H | -0.93344 | 3.82353 | -2.10815 |
| H | 0.50410 | 4.62726 | -1.44664 |
| H | 0.68063 | 3.15185 | -2.41548 |
| C | 1.32555 | 2.53025 | 0.17314 |
| H | 1.23758 | 1.92330 | 1.07821 |
| H | 1.93704 | 1.97869 | -0.54627 |
| H | 1.83385 | 3.46447 | 0.42582 |
| C | -0.95067 | 3.49060 | 0.62035 |
| H | -1.93969 | 3.68218 | 0.19693 |
| H | -1.06590 | 2.84485 | 1.49639 |
| H | -0.51860 | 4.43997 | 0.94624 |

36 13

**SM (Before SET): 36** in DMSO
26
-631.9734622

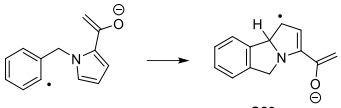
| | | | |
|---|---|---|---|
| C | -2.81274 | 1.23120 | -0.00306 |
| C | -1.57030 | 0.58300 | -0.00898 |
| C | -1.52182 | -0.83264 | -0.00126 |
| C | -2.67864 | -1.58706 | 0.01092 |
| C | -3.91864 | -0.93519 | 0.01658 |
| C | -3.97235 | 0.46187 | 0.00967 |
| H | -2.87069 | 2.31386 | -0.00842 |
| H | -4.83466 | -1.51320 | 0.02634 |
| H | -4.93694 | 0.95763 | 0.01429 |
| C | -0.07948 | -1.29990 | -0.01034 |
| H | 0.16786 | -1.89476 | 0.87690 |
| H | 0.14706 | -1.90473 | -0.89616 |
| N | 0.63819 | -0.03275 | -0.02423 |
| C | -0.22174 | 1.06473 | -0.01946 |
| C | 1.96950 | 0.38842 | -0.00513 |
| C | 0.55773 | 2.21821 | -0.00383 |
| C | 1.89838 | 1.81445 | 0.00483 |
| H | 2.76555 | 2.45638 | 0.01579 |
| H | 0.18547 | 3.23226 | 0.00206 |
| C | 3.15281 | -0.39387 | 0.00367 |
| C | 3.13156 | -1.90793 | -0.01216 |
| H | 3.75343 | -2.26585 | -0.83992 |
| H | 3.58188 | -2.29346 | 0.91006 |
| O | 4.30702 | 0.16634 | 0.03493 |
| H | -2.63111 | -2.67130 | 0.01680 |
| H | 2.14308 | -2.35012 | -0.11626 |

**Prod (After SET): 13** in DMSO
26
-631.8971159

| | | | |
|---|---|---|---|
| C | 2.77758 | 1.23734 | 0.00042 |
| C | 1.55750 | 0.57055 | 0.00004 |
| C | 1.50265 | -0.83030 | -0.00034 |
| C | 2.66276 | -1.58587 | -0.00039 |
| C | 3.88905 | -0.91886 | -0.00008 |
| C | 3.94406 | 0.47569 | 0.00033 |
| H | 2.81968 | 2.32001 | 0.00075 |
| H | 4.80888 | -1.49117 | -0.00014 |
| H | 4.90687 | 0.97253 | 0.00064 |
| C | 0.06398 | -1.29471 | -0.00031 |
| H | -0.17817 | -1.88003 | -0.88923 |
| H | -0.17774 | -1.88068 | 0.88831 |
| N | -0.65337 | -0.01546 | 0.00028 |
| C | 0.18581 | 1.05952 | 0.00028 |
| C | -1.96169 | 0.42255 | -0.00032 |
| C | -0.56971 | 2.22445 | -0.00015 |
| C | -1.91551 | 1.81635 | -0.00054 |
| H | -2.78963 | 2.44927 | -0.00085 |
| H | -0.18919 | 3.23321 | -0.00021 |
| C | -3.16157 | -0.41459 | 0.00011 |
| C | -3.00852 | -1.91493 | 0.00044 |
| H | -3.99602 | -2.37149 | 0.00011 |
| H | -2.45653 | -2.24442 | -0.88283 |
| O | -4.26746 | 0.10390 | 0.00014 |
| H | 2.62413 | -2.66916 | -0.00070 |
| H | -2.45724 | -2.24411 | 0.88425 |

**TS: 31** cyclisation to form **S29** in DMSO
26
-631.8883080

| | | | |
|---|---|---|---|
| C | 2.72254 | 1.06651 | 0.58404 |
| C | 1.57975 | 0.73495 | -0.11500 |
| C | 1.30112 | -0.54739 | -0.55007 |
| C | 2.21671 | -1.56087 | -0.26378 |
| C | 3.37980 | -1.26029 | 0.44583 |
| C | 3.63411 | 0.04254 | 0.87047 |
| H | 2.91989 | 2.08188 | 0.91313 |
| H | 4.08861 | -2.04836 | 0.67206 |
| H | 4.53886 | 0.26518 | 1.42602 |
| C | 0.00239 | -0.75238 | -1.30916 |
| H | 0.17841 | -0.73528 | -2.38878 |
| H | -0.47891 | -1.69366 | -1.05367 |
| N | -0.87826 | 0.35711 | -0.94990 |
| C | -0.32417 | 1.63025 | -1.01003 |
| C | -1.78869 | 0.32265 | 0.09352 |
| C | -1.00684 | 2.44000 | -0.10199 |
| H | 0.26876 | 1.92094 | -1.86452 |
| C | -1.89236 | 1.60598 | 0.60962 |
| H | -2.57539 | 1.89488 | 1.39336 |
| H | -0.86892 | 3.50415 | 0.01521 |
| C | -2.59390 | -0.87409 | 0.51180 |
| C | -2.95890 | -1.76918 | -0.46443 |
| H | -2.69341 | -1.61564 | -1.50220 |
| H | -3.56939 | -2.62835 | -0.20889 |
| O | -2.91425 | -0.91728 | 1.75385 |
| H | 2.02390 | -2.57947 | -0.58804 |

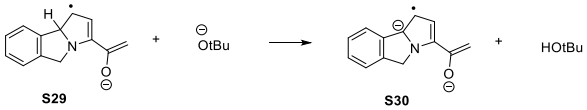



**SM: 31** cyclisation to form **S29** in DMSO
26
-631.9002517

| | | | |
|---|---|---|---|
| C | 2.79905 | -0.94212 | -1.21862 |
| C | 1.64483 | -0.88465 | -0.47479 |
| C | 1.41100 | -0.04832 | 0.59319 |
| C | 2.45850 | 0.81601 | 0.93481 |
| C | 3.65316 | 0.80191 | 0.21883 |
| C | 3.82960 | -0.07003 | -0.85450 |
| H | 2.91357 | -1.62825 | -2.05002 |
| H | 4.45043 | 1.48113 | 0.49604 |
| H | 4.76029 | -0.07251 | -1.41012 |
| C | 0.11410 | -0.05963 | 1.37513 |
| H | 0.24800 | -0.64684 | 2.28790 |
| H | -0.15433 | 0.95661 | 1.66141 |
| N | -0.98909 | -0.64177 | 0.63177 |
| C | -1.19529 | -1.99708 | 0.56976 |
| C | -1.97525 | 0.00916 | -0.08416 |
| C | -2.32234 | -2.23322 | -0.18305 |
| H | -0.52997 | -2.67246 | 1.08612 |
| C | -2.81909 | -0.96576 | -0.58567 |
| H | -3.69436 | -0.76165 | -1.18275 |
| H | -2.74027 | -3.20307 | -0.40580 |
| C | -2.11464 | 1.49400 | -0.29380 |
| C | -0.98146 | 2.25365 | -0.45588 |
| H | 0.00783 | 1.81835 | -0.47803 |
| H | -1.07650 | 3.31931 | -0.63549 |
| O | -3.32524 | 1.91869 | -0.35002 |
| H | 2.32792 | 1.50875 | 1.76100 |

**Prod: S29** cyclised in DMSO
26
-631.9403183

| | | | |
|---|---|---|---|
| C | -2.66979 | 1.11985 | 0.01693 |
| C | -1.47624 | 0.49287 | 0.35042 |
| C | -1.31460 | -0.87755 | 0.17675 |
| C | -2.34952 | -1.65169 | -0.33409 |
| C | -3.54937 | -1.02799 | -0.67491 |
| C | -3.70842 | 0.34758 | -0.50136 |
| H | -2.79295 | 2.18945 | 0.15131 |
| H | -4.36455 | -1.61541 | -1.08122 |
| H | -4.64567 | 0.81878 | -0.77377 |
| C | 0.06615 | -1.30018 | 0.62038 |
| H | 0.02062 | -1.89715 | 1.53734 |
| H | 0.59490 | -1.88525 | -0.13274 |
| N | 0.77067 | -0.02375 | 0.85557 |
| C | -0.20955 | 1.09431 | 0.92641 |
| C | 1.80879 | 0.36653 | -0.00791 |
| C | 0.44430 | 2.19180 | 0.13282 |
| H | -0.38964 | 1.39414 | 1.96897 |
| C | 1.60536 | 1.70362 | -0.40407 |
| H | 2.31101 | 2.24443 | -1.01798 |
| H | 0.03938 | 3.18952 | 0.04578 |
| C | 3.00379 | -0.44954 | -0.32210 |
| C | 3.24492 | -1.56927 | 0.44734 |
| H | 2.59917 | -1.84348 | 1.27097 |
| H | 4.12585 | -2.17248 | 0.25592 |
| O | 3.74507 | -0.02217 | -1.28775 |
| H | -2.22831 | -2.72094 | -0.47122 |




S29 S30

**SM: S29** + tert-butoxide anion in DMSO
40
-865.0661243

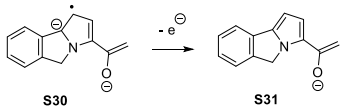
| | | | |
|---|---|---|---|
| C | -1.66618 | -2.45343 | 0.95276 |
| C | -1.37281 | -1.26848 | 0.29004 |
| C | -2.20263 | -0.79195 | -0.72048 |
| C | -3.34559 | -1.49336 | -1.08628 |
| C | -3.64871 | -2.68051 | -0.41925 |
| C | -2.81530 | -3.15716 | 0.59339 |
| H | -1.01645 | -2.82362 | 1.73899 |
| H | -4.53960 | -3.23641 | -0.68798 |
| H | -3.06393 | -4.08032 | 1.10406 |
| C | -1.64984 | 0.49779 | -1.28284 |
| H | -1.29223 | 0.35746 | -2.30880 |
| H | -2.38167 | 1.30711 | -1.29470 |
| N | -0.53592 | 0.83173 | -0.37506 |
| C | -0.19229 | -0.34176 | 0.47853 |
| C | -0.60908 | 1.96615 | 0.44564 |
| C | 0.00221 | 0.26353 | 1.84086 |
| H | 0.72721 | -0.83339 | 0.11083 |
| C | -0.25552 | 1.60702 | 1.76314 |
| H | -0.17656 | 2.32633 | 2.56592 |
| H | 0.33526 | -0.29582 | 2.70349 |
| C | -0.87825 | 3.34052 | -0.03528 |
| C | -0.80508 | 3.57285 | -1.39426 |
| H | -0.97755 | 4.57078 | -1.78228 |
| O | -1.14063 | 4.22454 | 0.86857 |
| H | -3.99527 | -1.12617 | -1.87374 |
| H | -0.53906 | 2.78684 | -2.08859 |
| O | 2.51284 | -1.67724 | -0.88328 |
| C | 3.48134 | -0.87811 | -0.32388 |
| C | 4.86594 | -1.14433 | -0.95837 |
| H | 4.81856 | -0.94779 | -2.03442 |
| H | 5.65687 | -0.51946 | -0.52706 |
| H | 5.13909 | -2.19513 | -0.81621 |
| C | 3.60260 | -1.13642 | 1.19624 |
| H | 2.63998 | -0.93235 | 1.67578 |
| H | 3.85657 | -2.18753 | 1.36933 |
| H | 4.36695 | -0.51250 | 1.67443 |
| C | 3.15827 | 0.62389 | -0.51718 |
| H | 3.07038 | 0.84380 | -1.58697 |
| H | 2.20091 | 0.86297 | -0.04295 |
| H | 3.92976 | 1.27719 | -0.09269 |

**TS: S29** + tert-butoxide anion in DMSO
40
-865.0544641

| | | | |
|---|---|---|---|
| C | -0.97476 | 2.33664 | 0.99465 |
| C | -0.07487 | 1.48834 | 0.34934 |
| C | 0.87305 | 2.02601 | -0.53162 |
| C | 0.92694 | 3.38856 | -0.78428 |
| C | 0.02167 | 4.23632 | -0.14028 |
| C | -0.91820 | 3.70842 | 0.74562 |
| H | -1.71000 | 1.93691 | 1.68510 |
| H | 0.05228 | 5.30380 | -0.32502 |
| H | -1.61272 | 4.37321 | 1.24777 |
| C | 1.74105 | 0.92231 | -1.09381 |
| H | 1.61957 | 0.83517 | -2.18037 |
| H | 2.80541 | 1.08121 | -0.89775 |
| N | 1.26453 | -0.28283 | -0.39848 |
| C | 0.04009 | 0.00878 | 0.38816 |
| C | 2.11033 | -1.10121 | 0.36419 |
| C | 0.25251 | -0.72705 | 1.65108 |
| H | -0.99487 | -0.47468 | -0.28785 |
| C | 1.46248 | -1.38496 | 1.58359 |
| H | 1.87126 | -2.06113 | 2.32219 |
| H | -0.47106 | -0.78670 | 2.45316 |
| C | 3.37196 | -1.69723 | -0.11471 |
| C | 3.69316 | -1.58809 | -1.45781 |
| H | 3.03268 | -1.10398 | -2.16482 |
| O | 4.09676 | -2.30451 | 0.77035 |
| H | 1.66540 | 3.79587 | -1.46810 |
| O | -1.93436 | -0.93631 | -1.09227 |
| C | -3.03030 | -1.43068 | -0.38231 |
| C | -4.20294 | -1.64936 | -1.34783 |
| H | -3.91179 | -2.35495 | -2.13121 |
| H | -5.08498 | -2.04577 | -0.83380 |
| H | -4.47483 | -0.70224 | -1.82274 |
| C | -3.46735 | -0.43528 | 0.70835 |
| H | -2.66005 | -0.29225 | 1.43227 |
| H | -3.69525 | 0.53459 | 0.25592 |
| H | -4.35388 | -0.78644 | 1.24618 |
| C | -2.67637 | -2.77033 | 0.28700 |
| H | -2.38360 | -3.49813 | -0.47578 |
| H | -1.83166 | -2.62777 | 0.96764 |
| H | -3.51791 | -3.18201 | 0.85425 |
| H | 4.61430 | -2.02550 | -1.82836 |

**Prod: S30** + tert-butanol in DMSO
40
-865.0879020

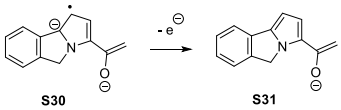
| | | | |
|---|---|---|---|
| C | 2.91802 | -0.09566 | 1.26263 |
| C | 1.72101 | -0.65361 | 0.70176 |
| C | 1.80837 | -1.32326 | -0.56759 |
| C | 2.99342 | -1.45832 | -1.23810 |
| C | 4.19169 | -0.91232 | -0.66919 |
| C | 4.10790 | -0.23978 | 0.56808 |
| H | 2.89452 | 0.43226 | 2.21060 |
| H | 5.14019 | -1.00970 | -1.18224 |
| H | 5.01414 | 0.18253 | 0.99544 |
| C | 0.42051 | -1.79466 | -0.97476 |
| H | 0.05728 | -1.29849 | -1.88294 |
| H | 0.38076 | -2.87484 | -1.14416 |
| N | -0.38458 | -1.40381 | 0.18173 |
| C | 0.37015 | -0.69783 | 1.12212 |
| C | -1.74582 | -1.32603 | 0.48821 |
| C | -0.52353 | -0.21128 | 2.08946 |
| H | -0.96266 | 0.90487 | -0.17437 |
| C | -1.82447 | -0.60931 | 1.67456 |
| H | -2.75450 | -0.40589 | 2.18414 |
| H | -0.26710 | 0.37893 | 2.95666 |
| C | -2.88297 | -1.91247 | -0.27096 |
| C | -2.64472 | -2.67903 | -1.39580 |
| H | -3.48883 | -3.09794 | -1.93325 |
| H | -1.65354 | -2.89909 | -1.76021 |
| O | -4.05696 | -1.65028 | 0.19479 |
| H | 3.02883 | -1.96820 | -2.19730 |
| O | -0.98855 | 1.52027 | -0.92156 |
| C | -0.63886 | 2.82377 | -0.43899 |
| C | -0.75905 | 3.75264 | -1.63927 |
| H | -1.78146 | 3.74394 | -2.02440 |
| H | -0.50116 | 4.77584 | -1.35731 |
| H | -0.08324 | 3.42972 | -2.43481 |
| C | 0.79350 | 2.80445 | 0.09163 |
| H | 0.88213 | 2.08727 | 0.91199 |
| H | 1.48355 | 2.49993 | -0.70000 |
| H | 1.08597 | 3.79491 | 0.45015 |
| C | -1.61361 | 3.23264 | 0.66422 |
| H | -2.63752 | 3.23022 | 0.28211 |
| H | -1.54905 | 2.52711 | 1.49760 |
| H | -1.38149 | 4.23379 | 1.03613 |




S30 S31

**SM (Before SET): S30** in DMSO
25
-631.4374431

| | | | |
|---|---|---|---|
| C | -2.79124 | 1.26514 | -0.03428 |
| C | -1.52033 | 0.59767 | -0.01463 |
| C | -1.50643 | -0.84003 | 0.03415 |
| C | -2.65735 | -1.57863 | 0.06318 |
| C | -3.92635 | -0.90930 | 0.05628 |
| C | -3.94576 | 0.50111 | 0.00413 |
| H | -2.85017 | 2.34808 | -0.07328 |
| H | -4.84929 | -1.47497 | 0.07621 |
| H | -4.90616 | 1.01074 | -0.00693 |
| C | -0.06235 | -1.31783 | 0.05460 |
| H | 0.20737 | -1.80693 | 0.99987 |
| H | 0.15109 | -2.02042 | -0.75538 |
| N | 0.67435 | -0.06519 | -0.10493 |
| C | -0.17549 | 1.04143 | -0.07918 |
| C | 2.00643 | 0.34087 | 0.00070 |
| C | 0.63440 | 2.18704 | -0.04995 |
| C | 1.97854 | 1.72837 | 0.01005 |
| H | 2.86933 | 2.33883 | 0.03823 |
| H | 0.29246 | 3.21106 | -0.03223 |
| C | 3.21748 | -0.52175 | 0.01397 |
| C | 3.10427 | -1.88389 | -0.19345 |
| H | 2.16240 | -2.37461 | -0.38345 |
| H | 4.00222 | -2.49267 | -0.18194 |
| O | 4.33494 | 0.09001 | 0.21968 |
| H | -2.61412 | -2.66400 | 0.10238 |

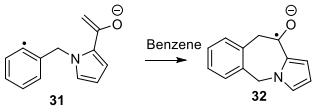


S30 S31

**Prod (After SET): S31** in DMSO
25
-631.3942397

| | | | |
|---|---|---|---|
| C | 2.74636 | 1.25209 | 0.01558 |
| C | 1.53102 | 0.57328 | 0.01894 |
| C | 1.49907 | -0.83073 | -0.01366 |
| C | 2.67026 | -1.56790 | -0.04680 |
| C | 3.89022 | -0.88731 | -0.05001 |
| C | 3.92389 | 0.50736 | -0.01907 |
| H | 2.77656 | 2.33524 | 0.03913 |
| H | 4.81741 | -1.44709 | -0.07678 |
| H | 4.87920 | 1.01919 | -0.02248 |
| C | 0.06721 | -1.31760 | 0.00484 |
| H | -0.19168 | -1.90664 | -0.87862 |
| H | -0.14328 | -1.91596 | 0.89487 |
| N | -0.67293 | -0.05751 | 0.03138 |
| C | 0.15578 | 1.04304 | 0.04473 |
| C | -1.98882 | 0.33877 | 0.01475 |
| C | -0.62745 | 2.17983 | 0.04665 |
| C | -1.97294 | 1.72961 | 0.02603 |
| H | -2.86385 | 2.33760 | 0.01929 |
| H | -0.27532 | 3.19978 | 0.05542 |
| C | -3.20803 | -0.53368 | -0.02024 |
| C | -3.07542 | -1.89403 | 0.13286 |
| H | -2.12949 | -2.38357 | 0.30019 |
| H | -3.96596 | -2.51251 | 0.11165 |
| O | -4.31315 | 0.09649 | -0.18993 |
| H | 2.64520 | -2.65177 | -0.07051 |

## 6.2 Benzene (Scheme S2.2)




31 32

**SM: 31** cyclisation to **32** in Benzene

26

-631.8573282

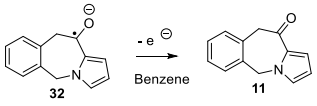
| | | | |
|---|---|---|---|
| C | 2.73158 | 0.13430 | 1.48264 |
| C | 1.51391 | 0.22203 | 0.81044 |
| C | 1.44844 | 0.03122 | -0.57467 |
| C | 2.64705 | -0.24167 | -1.19640 |
| C | 3.87385 | -0.34112 | -0.58997 |
| C | 3.90960 | -0.14513 | 0.79548 |
| H | 2.75716 | 0.28290 | 2.55568 |
| H | 0.59713 | 0.43491 | 1.35254 |
| H | 4.77653 | -0.56119 | -1.14864 |
| H | 4.85231 | -0.21272 | 1.32688 |
| C | 0.14597 | 0.09761 | -1.34899 |
| H | 0.29848 | 0.69261 | -2.25338 |
| H | -0.15469 | -0.90869 | -1.64472 |
| N | -0.93582 | 0.68359 | -0.58618 |
| C | -1.05561 | 2.04109 | -0.40674 |
| C | -1.98223 | 0.03644 | 0.04562 |
| C | -2.18600 | 2.27948 | 0.33887 |
| H | -0.32832 | 2.71378 | -0.83597 |
| C | -2.77379 | 1.01631 | 0.61300 |
| H | -3.68112 | 0.80927 | 1.15791 |
| H | -2.54812 | 3.25084 | 0.64002 |
| C | -2.24024 | -1.45337 | 0.10031 |
| C | -1.16059 | -2.30278 | 0.21461 |
| H | -0.14894 | -1.94008 | 0.33726 |
| H | -1.33609 | -3.36978 | 0.29306 |
| O | -3.47065 | -1.77794 | 0.07717 |

**Prod: 32** cyclised in Benzene

26

-631.9298533

| | | | |
|---|---|---|---|
| C | 3.17523 | -1.14539 | -0.68892 |
| C | 2.04985 | -1.59794 | -0.00470 |
| C | 1.13565 | -0.69948 | 0.53888 |
| C | 1.33234 | 0.68461 | 0.39034 |
| C | 2.45978 | 1.12538 | -0.30600 |
| C | 3.37675 | 0.22414 | -0.83958 |
| H | 3.88429 | -1.85406 | -1.10153 |
| H | 1.87573 | -2.66405 | 0.10669 |
| H | 2.61632 | 2.19211 | -0.43076 |
| H | 4.24772 | 0.59087 | -1.37156 |
| C | -0.12269 | -1.17707 | 1.21786 |
| H | -0.08572 | -2.25818 | 1.36138 |
| H | -0.22953 | -0.71662 | 2.20770 |
| N | -1.29339 | -0.88635 | 0.41181 |
| C | -2.18576 | -1.85133 | -0.02542 |
| C | -1.67855 | 0.37235 | -0.07086 |
| C | -3.15314 | -1.22641 | -0.78276 |
| H | -2.04792 | -2.88648 | 0.24501 |
| C | -2.85485 | 0.15462 | -0.82131 |
| H | -3.39497 | 0.93413 | -1.33395 |
| H | -3.98684 | -1.72317 | -1.25813 |
| C | -1.00606 | 1.61084 | 0.15835 |
| C | 0.31526 | 1.65038 | 0.93878 |
| H | 0.16249 | 1.46830 | 2.01243 |
| H | 0.68821 | 2.67067 | 0.84013 |
| O | -1.46737 | 2.71285 | -0.29852 |



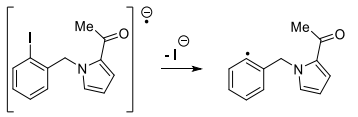

32 11

**Prod (After SET): 11** in Benzene

26

-631.8918340

| | | | |
|---|---|---|---|
| C | 3.23064 | -1.12431 | -0.66784 |
| C | 2.07944 | -1.60437 | -0.04983 |
| C | 1.13720 | -0.72204 | 0.46933 |
| C | 1.34376 | 0.65916 | 0.37379 |
| C | 2.49472 | 1.13187 | -0.25118 |
| C | 3.43646 | 0.24634 | -0.76882 |
| H | 3.95927 | -1.81827 | -1.06944 |
| H | 1.91070 | -2.67324 | 0.02802 |
| H | 2.65582 | 2.20143 | -0.33029 |
| H | 4.32873 | 0.62958 | -1.24932 |
| C | -0.11679 | -1.22885 | 1.13511 |
| H | -0.09030 | -2.31437 | 1.22071 |
| H | -0.21068 | -0.81847 | 2.14516 |
| N | -1.31867 | -0.89163 | 0.37258 |
| C | -2.24278 | -1.80317 | -0.02372 |
| C | -1.70806 | 0.36025 | -0.07390 |
| C | -3.24285 | -1.15749 | -0.72921 |
| H | -2.11959 | -2.84656 | 0.22241 |
| C | -2.90341 | 0.20585 | -0.76111 |
| H | -3.44475 | 1.01490 | -1.22572 |
| H | -4.10790 | -1.62805 | -1.16783 |
| C | -0.98776 | 1.61979 | 0.14001 |
| C | 0.31687 | 1.61667 | 0.92852 |
| H | 0.08042 | 1.35749 | 1.96755 |
| H | 0.69213 | 2.63896 | 0.91719 |
| O | -1.43097 | 2.66248 | -0.29917 |




33 34

**TS: 33** C-I elongation to give **34** in Benzene

28

-643.8878222

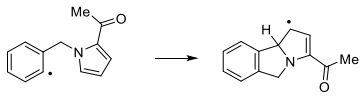
| | | | |
|---|---|---|---|
| C | 0.45728 | 2.99938 | 0.30352 |
| C | 0.90343 | 1.77418 | -0.17821 |
| C | 0.07523 | 0.69032 | -0.31691 |
| C | -1.29197 | 0.91209 | 0.04184 |
| C | -1.77325 | 2.12042 | 0.52019 |
| C | -0.87703 | 3.17629 | 0.65589 |
| H | 1.19856 | 3.81734 | 0.40937 |
| H | 1.94275 | 1.63856 | -0.44631 |
| H | -2.81633 | 2.23819 | 0.78252 |
| H | -1.22733 | 4.12906 | 1.03573 |
| C | 0.51819 | -0.65123 | -0.84581 |
| H | 0.12785 | -1.44320 | -0.20897 |
| H | 0.08527 | -0.81232 | -1.83820 |
| N | 1.95058 | -0.74485 | -0.97010 |
| C | 2.87093 | -0.59906 | 0.09810 |
| C | 2.56768 | -0.32506 | -2.15406 |
| C | 4.06814 | -0.11644 | -0.47768 |
| C | 3.86290 | 0.03537 | -1.86775 |
| H | 2.02123 | -0.34487 | -3.08433 |
| H | 4.97636 | 0.05317 | 0.07748 |
| H | 4.59382 | 0.35627 | -2.59660 |
| C | 2.63912 | -0.87845 | 1.47426 |
| C | 1.38307 | -1.60322 | 1.93405 |
| H | 0.48767 | -0.96600 | 1.94220 |
| H | 1.15688 | -2.48337 | 1.32090 |
| O | 3.51747 | -0.57895 | 2.35256 |
| I | -2.79249 | -0.74732 | -0.14162 |
| H | 1.56055 | -1.93659 | 2.95759 |

**Prod: 34** + Iodide anion in Benzene

28

-643.9288407

| | | | |
|---|---|---|---|
| C | 1.26617 | 3.30715 | 0.52518 |
| C | 1.52459 | 2.08200 | -0.08792 |
| C | 0.46754 | 1.25222 | -0.47816 |
| C | -0.81080 | 1.70704 | -0.22854 |
| C | -1.11079 | 2.90370 | 0.37787 |
| C | -0.04264 | 3.72196 | 0.75930 |
| H | 2.09477 | 3.93655 | 0.82826 |
| H | 2.55015 | 1.76249 | -0.25237 |
| H | -2.13815 | 3.19708 | 0.56385 |
| H | -0.23351 | 4.67305 | 1.24450 |
| C | 0.68077 | -0.08546 | -1.15550 |
| H | -0.05604 | -0.80113 | -0.79415 |
| H | 0.51371 | 0.01391 | -2.23011 |
| N | 2.03961 | -0.59232 | -0.98916 |
| C | 2.66147 | -1.02701 | 0.17030 |
| C | 2.98190 | -0.45412 | -1.96024 |
| C | 4.01074 | -1.17910 | -0.11282 |
| C | 4.21582 | -0.82113 | -1.45825 |
| H | 2.69862 | -0.09610 | -2.93816 |
| H | 4.73801 | -1.53727 | 0.59864 |
| H | 5.14281 | -0.83548 | -2.00888 |
| C | 2.04779 | -1.33503 | 1.47953 |
| C | 0.55202 | -1.40383 | 1.64309 |
| H | 0.08087 | -0.43394 | 1.46402 |
| H | 0.11003 | -2.10911 | 0.93530 |
| O | 2.78585 | -1.56912 | 2.42114 |
| I | -3.07672 | -0.78031 | -0.17658 |
| H | 0.33345 | -1.72506 | 2.65966 |




**34** **35**

**SM: 34** cyclisation to **35** in Benzene

27

-632.3967710

| | | | |
|---|---|---|---|
| C | -2.25152 | -0.19440 | 1.70366 |
| C | -1.21279 | -0.46335 | 0.84550 |
| C | -1.28790 | -0.48055 | -0.52763 |
| C | -2.54304 | -0.20373 | -1.08291 |
| C | -3.63284 | 0.06860 | -0.26188 |
| C | -3.49424 | 0.07599 | 1.12534 |
| H | -2.11853 | -0.18867 | 2.77913 |
| H | -4.59701 | 0.28184 | -0.70738 |
| H | -4.34691 | 0.29609 | 1.75723 |
| C | -0.09308 | -0.77975 | -1.40788 |
| H | -0.22027 | -1.75524 | -1.88131 |
| H | -0.01968 | -0.04592 | -2.21073 |
| N | 1.15246 | -0.83891 | -0.65787 |
| C | 1.72528 | -2.02565 | -0.31099 |
| C | 1.77839 | 0.17584 | 0.05326 |
| C | 2.74338 | -1.79637 | 0.59086 |
| H | 1.35351 | -2.94864 | -0.72930 |
| C | 2.77163 | -0.40825 | 0.82241 |
| H | 3.44581 | 0.14609 | 1.45600 |
| H | 3.38946 | -2.54629 | 1.01790 |
| C | 1.51834 | 1.62660 | -0.00269 |
| C | 0.64750 | 2.22247 | -1.08483 |
| H | -0.39396 | 1.91917 | -0.95340 |
| H | 0.71376 | 3.30622 | -1.01198 |
| O | 2.04891 | 2.34991 | 0.81898 |
| H | -2.66073 | -0.19720 | -2.16269 |
| H | 0.98135 | 1.90101 | -2.07358 |

**TS: 34** cyclisation to **35** in Benzene

27

-632.3816047

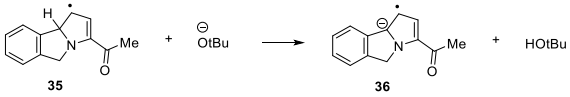
| | | | |
|---|---|---|---|
| C | -2.75247 | 1.07209 | -0.54556 |
| C | -1.62043 | 0.70381 | 0.14435 |
| C | -1.32387 | -0.59048 | 0.51787 |
| C | -2.22573 | -1.59567 | 0.17117 |
| C | -3.38469 | -1.26664 | -0.53064 |
| C | -3.64909 | 0.05371 | -0.88880 |
| H | -2.94935 | 2.10168 | -0.82354 |
| H | -4.08309 | -2.04766 | -0.80626 |
| H | -4.55070 | 0.29508 | -1.44073 |
| C | -0.03047 | -0.80146 | 1.28157 |
| H | -0.21248 | -0.81269 | 2.35982 |
| H | 0.45063 | -1.73693 | 1.01080 |
| N | 0.83435 | 0.33746 | 0.96646 |
| C | 0.24645 | 1.58477 | 1.07730 |
| C | 1.72017 | 0.38448 | -0.10395 |
| C | 0.88292 | 2.45844 | 0.18988 |
| H | -0.35579 | 1.82128 | 1.94242 |
| C | 1.77881 | 1.69295 | -0.56548 |
| H | 2.45314 | 2.03208 | -1.33641 |
| H | 0.70660 | 3.52016 | 0.12177 |
| C | 2.60300 | -0.70166 | -0.55504 |
| C | 2.84567 | -1.90392 | 0.33228 |
| H | 2.18534 | -2.72113 | 0.02875 |
| H | 3.87180 | -2.23349 | 0.17382 |
| O | 3.18060 | -0.60101 | -1.62166 |
| H | -2.02516 | -2.62843 | 0.44028 |
| H | 2.68213 | -1.68651 | 1.38763 |

**Prod: 35** in Benzene

27

-632.4429452

| | | | |
|---|---|---|---|
| C | -2.72298 | 1.11329 | 0.03468 |
| C | -1.51483 | 0.49814 | 0.33099 |
| C | -1.34520 | -0.87083 | 0.15554 |
| C | -2.38629 | -1.65687 | -0.31986 |
| C | -3.60054 | -1.04472 | -0.62430 |
| C | -3.76743 | 0.32891 | -0.44974 |
| H | -2.85362 | 2.18112 | 0.17199 |
| H | -4.42220 | -1.64094 | -1.00286 |
| H | -4.71694 | 0.78997 | -0.69416 |
| C | 0.05380 | -1.28653 | 0.54820 |
| H | 0.05541 | -1.89660 | 1.45621 |
| H | 0.55472 | -1.84421 | -0.24425 |
| N | 0.73556 | 0.00242 | 0.77614 |
| C | -0.24368 | 1.10951 | 0.87699 |
| C | 1.79361 | 0.42296 | -0.00804 |
| C | 0.40456 | 2.22056 | 0.09991 |
| H | -0.38844 | 1.40323 | 1.92644 |
| C | 1.58355 | 1.79278 | -0.39181 |
| H | 2.30145 | 2.35589 | -0.96953 |
| H | -0.01944 | 3.21127 | 0.01883 |
| C | 2.96830 | -0.35047 | -0.31893 |
| C | 3.17877 | -1.69093 | 0.35436 |
| H | 2.84637 | -2.49839 | -0.30395 |
| H | 4.24772 | -1.82030 | 0.52310 |
| O | 3.80647 | 0.09015 | -1.11064 |
| H | -2.25862 | -2.72476 | -0.45884 |
| H | 2.64309 | -1.76929 | 1.30107 |




35 36

**SM: 35** + tert-butoxide anion in Benzene

41

-865.5414505

| | | | |
|---|---|---|---|
| C | -1.44550 | 2.14282 | 1.20218 |
| C | -0.46990 | 1.40486 | 0.54401 |
| C | -0.05056 | 1.76949 | -0.73533 |
| C | -0.58781 | 2.87960 | -1.37119 |
| C | -1.55437 | 3.63362 | -0.70512 |
| C | -1.97912 | 3.26528 | 0.57140 |
| H | -1.79146 | 1.84179 | 2.18479 |
| H | -1.98229 | 4.50669 | -1.18410 |
| H | -2.73815 | 3.85348 | 1.07459 |
| C | 0.97265 | 0.78170 | -1.25232 |
| H | 0.58828 | 0.22957 | -2.11715 |
| H | 1.91159 | 1.26342 | -1.53727 |
| N | 1.18418 | -0.10652 | -0.10207 |
| C | 0.19817 | 0.13377 | 0.96416 |
| C | 2.41720 | -0.36217 | 0.46075 |
| C | 1.00953 | 0.04775 | 2.20293 |
| H | -0.63274 | -0.70828 | 1.00024 |
| C | 2.28358 | -0.28485 | 1.89227 |
| H | 3.09466 | -0.50253 | 2.57146 |
| H | 0.58449 | 0.12832 | 3.19393 |
| C | 3.59978 | -0.72149 | -0.25442 |
| C | 3.50356 | -1.00206 | -1.74351 |
| H | 2.49861 | -1.30275 | -2.04379 |
| H | 3.78981 | -0.11813 | -2.32134 |
| O | 4.69868 | -0.83155 | 0.32233 |
| H | -0.26541 | 3.15921 | -2.36884 |
| O | -1.80194 | -1.73305 | 1.05373 |
| C | -2.44472 | -2.05176 | -0.11914 |
| C | -2.50310 | -3.58342 | -0.29855 |
| H | -3.01634 | -4.02722 | 0.55951 |
| H | -3.02601 | -3.88167 | -1.21532 |
| H | -1.48485 | -3.98242 | -0.32812 |
| C | -1.71273 | -1.45246 | -1.34242 |
| H | -1.71620 | -0.35899 | -1.27261 |
| H | -0.67186 | -1.79358 | -1.34786 |
| H | -2.18439 | -1.73951 | -2.28923 |
| C | -3.88773 | -1.50449 | -0.11299 |
| H | -4.43372 | -1.93383 | 0.73232 |
| H | -3.85722 | -0.41807 | 0.01799 |
| H | -4.43337 | -1.73226 | -1.03670 |
| H | 4.20995 | -1.79790 | -1.98271 |

**Prod: 36** + tert-butanol in Benzene

41

-865.5881066

| | | | |
|---|---|---|---|
| C | 3.07456 | -0.36323 | 1.22371 |
| C | 1.85844 | -0.68374 | 0.59286 |
| C | 1.84017 | -0.87216 | -0.81774 |
| C | 2.98008 | -0.71865 | -1.57566 |
| C | 4.18879 | -0.38626 | -0.94197 |
| C | 4.21823 | -0.22044 | 0.44757 |
| H | 3.11643 | -0.21896 | 2.29762 |
| H | 5.09294 | -0.25910 | -1.52455 |
| H | 5.15610 | 0.03204 | 0.93151 |
| C | 0.44895 | -1.29671 | -1.24516 |
| H | 0.08808 | -0.76056 | -2.12604 |
| H | 0.40518 | -2.37710 | -1.45591 |
| N | -0.33467 | -0.98648 | -0.04337 |
| C | 0.53109 | -0.85633 | 1.06974 |
| C | -1.57286 | -1.50257 | 0.40823 |
| C | -0.20612 | -1.15018 | 2.22274 |
| H | -0.71292 | 0.84944 | -0.68056 |
| C | -1.48175 | -1.54714 | 1.82277 |
| H | -2.30731 | -1.82404 | 2.46116 |
| H | 0.16502 | -1.09603 | 3.23589 |
| C | -2.70802 | -1.75413 | -0.40275 |
| C | -2.63486 | -1.39762 | -1.88173 |
| H | -2.00273 | -2.09357 | -2.44238 |
| H | -3.64407 | -1.44668 | -2.29056 |
| O | -3.77635 | -2.22873 | 0.06309 |
| H | 2.94962 | -0.86359 | -2.65130 |
| H | -2.23607 | -0.38908 | -2.03103 |
| O | -0.87087 | 1.72001 | -1.08495 |
| C | -0.89221 | 2.67683 | -0.02434 |
| C | -1.38153 | 3.97789 | -0.64681 |
| H | -2.37949 | 3.83916 | -1.06910 |
| H | -1.42391 | 4.77121 | 0.10356 |
| H | -0.70582 | 4.28859 | -1.44749 |
| C | 0.52001 | 2.84334 | 0.53855 |
| H | 0.87325 | 1.89420 | 0.95166 |
| H | 1.20477 | 3.15091 | -0.25586 |
| H | 0.53828 | 3.59697 | 1.33119 |
| C | -1.84882 | 2.19590 | 1.06581 |
| H | -2.85024 | 2.05609 | 0.65053 |
| H | -1.50777 | 1.23755 | 1.47095 |
| H | -1.90372 | 2.91893 | 1.88444 |


36 13

**SM (Before SET): 36** in Benzene

26

-631.9360589

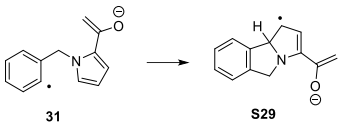
| | | | |
|---|---|---|---|
| C | -2.81716 | 1.23354 | -0.00400 |
| C | -1.56492 | 0.58968 | -0.01302 |
| C | -1.52384 | -0.83500 | -0.00138 |
| C | -2.67900 | -1.58470 | 0.01539 |
| C | -3.92532 | -0.93635 | 0.02282 |
| C | -3.97310 | 0.46364 | 0.01357 |
| H | -2.87836 | 2.31612 | -0.01101 |
| H | -4.84121 | -1.51430 | 0.03593 |
| H | -4.93751 | 0.96133 | 0.02032 |
| C | -0.08030 | -1.30179 | -0.01060 |
| H | 0.17357 | -1.89055 | 0.88109 |
| H | 0.14713 | -1.91489 | -0.89238 |
| N | 0.63616 | -0.03755 | -0.03630 |
| C | -0.22577 | 1.06055 | -0.02863 |
| C | 1.96818 | 0.38507 | -0.00609 |
| C | 0.56699 | 2.21633 | -0.00723 |
| C | 1.89738 | 1.80923 | 0.00670 |
| H | 2.77318 | 2.43951 | 0.02263 |
| H | 0.19959 | 3.23197 | -0.00018 |
| C | 3.16051 | -0.38584 | 0.00781 |
| C | 3.13624 | -1.90398 | -0.02166 |
| H | 3.76880 | -2.24570 | -0.84704 |
| H | 3.58245 | -2.28871 | 0.90182 |
| O | 4.30021 | 0.16506 | 0.05184 |
| H | -2.63010 | -2.66970 | 0.02409 |
| H | 2.14828 | -2.34511 | -0.13811 |

**Prod (After SET): 13** in Benzene

26

-631.8907121

| | | | |
|---|---|---|---|
| C | 2.77921 | 1.23558 | 0.00029 |
| C | 1.55803 | 0.57164 | 0.00007 |
| C | 1.50400 | -0.82922 | -0.00020 |
| C | 2.66317 | -1.58516 | -0.00033 |
| C | 3.89027 | -0.92015 | -0.00014 |
| C | 3.94510 | 0.47362 | 0.00018 |
| H | 2.82243 | 2.31812 | 0.00051 |
| H | 4.80969 | -1.49297 | -0.00026 |
| H | 4.90800 | 0.97024 | 0.00040 |
| C | 0.06407 | -1.29229 | 0.00005 |
| H | -0.17777 | -1.87927 | -0.88840 |
| H | -0.17702 | -1.87899 | 0.88894 |
| N | -0.65279 | -0.01517 | 0.00024 |
| C | 0.18717 | 1.06168 | 0.00026 |
| C | -1.96101 | 0.42310 | -0.00024 |
| C | -0.56941 | 2.22384 | -0.00014 |
| C | -1.91580 | 1.81474 | -0.00048 |
| H | -2.79342 | 2.44246 | -0.00085 |
| H | -0.19102 | 3.23321 | -0.00026 |
| C | -3.16535 | -0.41269 | 0.00009 |
| C | -3.01199 | -1.91596 | 0.00008 |
| H | -4.00145 | -2.36822 | -0.00002 |
| H | -2.46162 | -2.24595 | -0.88417 |
| O | -4.26696 | 0.10372 | 0.00021 |
| H | 2.62436 | -2.66863 | -0.00064 |
| H | -2.46169 | -2.24597 | 0.88436 |



31 S29

**SM: 31** cyclisation to form **S29** in Benzene

26

-631.8555478

| | | | |
|---|---|---|---|
| C | 3.01738 | -1.11400 | -0.91319 |
| C | 1.82597 | -1.04667 | -0.23348 |
| C | 1.41994 | -0.01870 | 0.58835 |
| C | 2.32281 | 1.04128 | 0.72970 |
| C | 3.55026 | 1.02566 | 0.07101 |
| C | 3.90264 | -0.04365 | -0.74917 |
| H | 3.26628 | -1.95393 | -1.55184 |
| H | 4.23032 | 1.86133 | 0.18692 |
| H | 4.85500 | -0.04520 | -1.26738 |
| C | 0.09421 | -0.02971 | 1.31940 |
| H | 0.20854 | -0.58354 | 2.25671 |
| H | -0.20300 | 0.99247 | 1.55125 |
| N | -0.97306 | -0.65175 | 0.56011 |
| C | -1.14079 | -2.01394 | 0.49373 |
| C | -2.00423 | -0.02259 | -0.11016 |
| C | -2.28719 | -2.27222 | -0.22227 |
| H | -0.43923 | -2.67447 | 0.98042 |
| C | -2.83561 | -1.01590 | -0.59110 |
| H | -3.73692 | -0.82389 | -1.15153 |
| H | -2.68288 | -3.25175 | -0.44442 |
| C | -2.18813 | 1.46733 | -0.28650 |
| C | -1.06305 | 2.22908 | -0.52280 |
| H | -0.08925 | 1.77869 | -0.66496 |
| H | -1.17122 | 3.29281 | -0.70364 |
| O | -3.39436 | 1.87020 | -0.23716 |
| H | 2.04335 | 1.89223 | 1.34394 |

**TS: 31** cyclisation to form **S29** in Benzene

26

-631.8456646

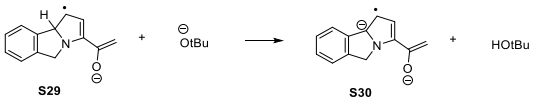
| | | | |
|---|---|---|---|
| C | 2.76532 | 1.07428 | 0.58402 |
| C | 1.60796 | 0.75090 | -0.09553 |
| C | 1.32297 | -0.53103 | -0.52810 |
| C | 2.24428 | -1.54477 | -0.26118 |
| C | 3.42106 | -1.24936 | 0.42617 |
| C | 3.68331 | 0.05166 | 0.85026 |
| H | 2.96615 | 2.08787 | 0.91724 |
| H | 4.13140 | -2.03997 | 0.63962 |
| H | 4.59704 | 0.27168 | 1.39273 |
| C | 0.01265 | -0.75382 | -1.26267 |
| H | 0.17690 | -0.77011 | -2.34524 |
| H | -0.46431 | -1.68820 | -0.97196 |
| N | -0.87425 | 0.35290 | -0.92476 |
| C | -0.34858 | 1.63546 | -0.99750 |
| C | -1.81789 | 0.31439 | 0.08642 |
| C | -1.06551 | 2.44093 | -0.11320 |
| H | 0.26159 | 1.92510 | -1.83945 |
| C | -1.95610 | 1.60211 | 0.58347 |
| H | -2.65997 | 1.87446 | 1.35398 |
| H | -0.94857 | 3.50891 | -0.00648 |
| C | -2.61506 | -0.89302 | 0.50763 |
| C | -2.93240 | -1.80414 | -0.47773 |
| H | -2.65999 | -1.63756 | -1.51216 |
| H | -3.55102 | -2.66049 | -0.23469 |
| O | -2.96269 | -0.91751 | 1.73076 |
| H | 2.03989 | -2.56350 | -0.57872 |

**Prod: S29** cyclised in Benzene

26

-631.8968615

| | | | |
|---|---|---|---|
| C | -2.67329 | 1.11582 | 0.01557 |
| C | -1.47728 | 0.49519 | 0.34985 |
| C | -1.31232 | -0.87553 | 0.17852 |
| C | -2.34628 | -1.65183 | -0.32996 |
| C | -3.54903 | -1.03383 | -0.67061 |
| C | -3.71156 | 0.34102 | -0.49950 |
| H | -2.79662 | 2.18639 | 0.14370 |
| H | -4.36197 | -1.62451 | -1.07736 |
| H | -4.64973 | 0.80987 | -0.77392 |
| C | 0.07203 | -1.29124 | 0.61779 |
| H | 0.02941 | -1.89564 | 1.53103 |
| H | 0.60784 | -1.86838 | -0.13709 |
| N | 0.76859 | -0.01557 | 0.85912 |
| C | -0.20996 | 1.10137 | 0.92144 |
| C | 1.81538 | 0.37177 | 0.00084 |
| C | 0.44701 | 2.19580 | 0.12408 |
| H | -0.39496 | 1.40439 | 1.96373 |
| C | 1.61371 | 1.70079 | -0.40373 |
| H | 2.32825 | 2.22451 | -1.02201 |
| H | 0.04373 | 3.19367 | 0.03092 |
| C | 3.00786 | -0.45417 | -0.32755 |
| C | 3.23978 | -1.56800 | 0.45897 |
| H | 2.60931 | -1.80509 | 1.30617 |
| H | 4.11839 | -2.17609 | 0.27588 |
| O | 3.72622 | -0.03784 | -1.30002 |
| H | -2.21986 | -2.72046 | -0.46897 |




S29 S30

**SM: S29** + tert-butoxide anion in Benzene
40
-864.9549963

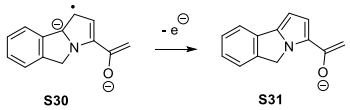
| | | | |
|---|---|---|---|
| C | 0.85455 | 1.06787 | -0.06983 |
| C | -0.47646 | 0.81097 | 0.24507 |
| C | -1.44999 | 1.80054 | 0.14536 |
| C | -1.11651 | 3.07752 | -0.29001 |
| C | 0.21150 | 3.34534 | -0.62276 |
| C | 1.18393 | 2.35052 | -0.50972 |
| H | 1.64902 | 0.32560 | 0.02139 |
| H | 0.49035 | 4.33499 | -0.96895 |
| H | 2.21730 | 2.56471 | -0.75955 |
| C | -2.79363 | 1.26870 | 0.58462 |
| H | -3.12815 | 1.75720 | 1.50748 |
| H | -3.57628 | 1.40855 | -0.16348 |
| N | -2.55906 | -0.17142 | 0.80055 |
| C | -1.10184 | -0.47177 | 0.75327 |
| C | -3.22539 | -1.10379 | -0.01773 |
| C | -1.01915 | -1.68885 | -0.12898 |
| H | -0.71359 | -0.68567 | 1.76122 |
| C | -2.28526 | -2.00733 | -0.54735 |
| H | -2.57679 | -2.83681 | -1.17571 |
| H | -0.09333 | -2.20394 | -0.34030 |
| C | -4.69759 | -1.17848 | -0.20120 |
| C | -5.48330 | -0.44367 | 0.67071 |
| H | -5.04795 | 0.13087 | 1.47794 |
| H | -6.56341 | -0.49387 | 0.58772 |
| O | -5.11535 | -1.94031 | -1.14293 |
| H | -1.87306 | 3.85173 | -0.37252 |
| O | 3.66166 | -0.21646 | 0.13167 |
| C | 4.91207 | -0.73971 | 0.05415 |
| C | 5.43281 | -1.16975 | 1.45087 |
| H | 5.43538 | -0.29758 | 2.11256 |
| H | 4.74787 | -1.91178 | 1.87298 |
| H | 6.44430 | -1.59635 | 1.42409 |
| C | 5.92020 | 0.29002 | -0.52166 |
| H | 5.92636 | 1.17797 | 0.11854 |
| H | 6.94416 | -0.09985 | -0.59510 |
| H | 5.58743 | 0.59461 | -1.51896 |
| C | 4.94628 | -1.98885 | -0.86457 |
| H | 4.25878 | -2.74238 | -0.46781 |
| H | 4.59541 | -1.70502 | -1.86170 |
| H | 5.94577 | -2.43452 | -0.95488 |

**TS: S29** + tert-butoxide anion in Benzene
40
-864.9392848

| | | | |
|---|---|---|---|
| C | -1.99798 | -2.10920 | 1.01013 |
| C | -1.49756 | -0.97287 | 0.37432 |
| C | -2.24758 | -0.36596 | -0.64397 |
| C | -3.47698 | -0.87451 | -1.02944 |
| C | -3.97801 | -2.01336 | -0.39010 |
| C | -3.23742 | -2.62025 | 0.62453 |
| H | -1.42512 | -2.59194 | 1.79555 |
| H | -4.93974 | -2.42181 | -0.68052 |
| H | -3.63075 | -3.50279 | 1.11901 |
| C | -1.50126 | 0.83499 | -1.18125 |
| H | -1.21188 | 0.67910 | -2.22895 |
| H | -2.08396 | 1.75936 | -1.13776 |
| N | -0.32615 | 0.93066 | -0.31076 |
| C | -0.20345 | -0.27201 | 0.54793 |
| C | -0.03518 | 2.07037 | 0.45070 |
| C | 0.21698 | 0.27911 | 1.85690 |
| H | 0.71139 | -1.10566 | 0.09016 |
| C | 0.32483 | 1.65177 | 1.74301 |
| H | 0.67022 | 2.34410 | 2.49862 |
| H | 0.48060 | -0.32604 | 2.71396 |
| C | 0.02682 | 3.45987 | -0.06817 |
| C | -0.00388 | 3.64390 | -1.44353 |
| H | -0.00124 | 2.80613 | -2.12907 |
| H | 0.06647 | 4.64863 | -1.84685 |
| O | 0.11626 | 4.39581 | 0.80779 |
| H | -4.05087 | -0.39171 | -1.81543 |
| O | 1.58865 | -1.98765 | -0.37859 |
| C | 2.88387 | -1.49131 | -0.33698 |
| C | 2.93206 | -0.01598 | -0.77986 |
| H | 2.50884 | 0.07950 | -1.78431 |
| H | 2.33177 | 0.60661 | -0.11024 |
| H | 3.95864 | 0.36845 | -0.79215 |
| C | 3.76980 | -2.32147 | -1.28193 |
| H | 3.38254 | -2.24572 | -2.30213 |
| H | 4.81266 | -1.98178 | -1.27480 |
| H | 3.73952 | -3.37366 | -0.98203 |
| C | 3.45460 | -1.59357 | 1.09185 |
| H | 2.83010 | -1.00349 | 1.76862 |
| H | 3.43072 | -2.63800 | 1.41939 |
| H | 4.48583 | -1.22626 | 1.15578 |

**Prod: S30** + tert-butanol in Benzene
40
-864.9792918

| | | | |
|---|---|---|---|
| C | 1.85336 | -1.64040 | 1.41101 |
| C | 0.61634 | -1.34843 | 0.73276 |
| C | 0.51133 | -1.65961 | -0.66167 |
| C | 1.54468 | -2.21504 | -1.36879 |
| C | 2.78265 | -2.51012 | -0.68871 |
| C | 2.88752 | -2.20717 | 0.68321 |
| H | 1.97785 | -1.41382 | 2.46467 |
| H | 3.62181 | -2.93307 | -1.22654 |
| H | 3.82539 | -2.41733 | 1.19270 |
| C | -0.87248 | -1.25756 | -1.15132 |
| H | -0.83630 | -0.51542 | -1.95608 |
| H | -1.44855 | -2.11732 | -1.51007 |
| N | -1.47349 | -0.69148 | 0.05250 |
| C | -0.60826 | -0.74429 | 1.13942 |
| C | -2.64179 | -0.01127 | 0.38461 |
| C | -1.24423 | -0.10852 | 2.20801 |
| H | 2.34709 | 0.16200 | -0.47327 |
| C | -2.50515 | 0.34244 | 1.71614 |
| H | -3.27096 | 0.87552 | 2.25909 |
| H | -0.84054 | 0.02579 | 3.20069 |
| C | -3.82106 | 0.27846 | -0.49153 |
| C | -3.84374 | -0.20410 | -1.78968 |
| H | -3.05378 | -0.80607 | -2.21048 |
| H | -4.70770 | 0.01444 | -2.40856 |
| O | -4.74914 | 0.97433 | 0.04908 |
| H | 1.43910 | -2.42182 | -2.43013 |
| O | 2.76675 | 0.98802 | -0.75860 |
| C | 2.00604 | 2.09308 | -0.26900 |
| C | 0.58667 | 2.05101 | -0.83415 |
| H | 0.61954 | 1.99629 | -1.92566 |
| H | 0.04784 | 1.18179 | -0.44997 |
| H | 0.02510 | 2.94349 | -0.54386 |
| C | 2.74485 | 3.33156 | -0.76400 |
| H | 2.78707 | 3.33003 | -1.85617 |
| H | 2.23551 | 4.23999 | -0.43330 |
| H | 3.76717 | 3.33858 | -0.37704 |
| C | 1.96609 | 2.06123 | 1.25842 |
| H | 1.45438 | 1.15634 | 1.59596 |
| H | 2.98313 | 2.06694 | 1.66023 |
| H | 1.42360 | 2.92764 | 1.64789 |




S30 S31

**SM (Before SET): S30** in Benzene
25
-631.3230920

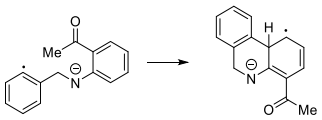
| | | | |
|---|---|---|---|
| C | -2.79616 | 1.26861 | 0.00015 |
| C | -1.52389 | 0.59435 | 0.00004 |
| C | -1.51194 | -0.83559 | -0.00005 |
| C | -2.66046 | -1.58186 | -0.00015 |
| C | -3.93709 | -0.90684 | -0.00020 |
| C | -3.95083 | 0.50225 | 0.00006 |
| H | -2.85190 | 2.35223 | 0.00036 |
| H | -4.86243 | -1.47021 | -0.00020 |
| H | -4.91169 | 1.01378 | 0.00010 |
| C | -0.06641 | -1.31351 | -0.00001 |
| H | 0.17602 | -1.91101 | 0.88519 |
| H | 0.17614 | -1.91105 | -0.88515 |
| N | 0.67585 | -0.05781 | -0.00000 |
| C | -0.17135 | 1.04350 | 0.00005 |
| C | 2.00992 | 0.34145 | -0.00004 |
| C | 0.63535 | 2.18530 | 0.00006 |
| C | 1.98545 | 1.72613 | 0.00002 |
| H | 2.88326 | 2.32595 | -0.00012 |
| H | 0.29084 | 3.20876 | 0.00017 |
| C | 3.23170 | -0.52363 | -0.00003 |
| C | 3.09615 | -1.90294 | 0.00040 |
| H | 2.14214 | -2.40623 | 0.00069 |
| H | 3.99521 | -2.51046 | 0.00041 |
| O | 4.35035 | 0.09968 | -0.00038 |
| H | -2.61396 | -2.66783 | -0.00023 |

**Prod (After SET): S31** in Benzene
25
-631.3512135

| | | | |
|---|---|---|---|
| C | 2.74842 | 1.25041 | 0.01241 |
| C | 1.52881 | 0.57753 | 0.01708 |
| C | 1.49794 | -0.82908 | -0.01138 |
| C | 2.66811 | -1.56564 | -0.04115 |
| C | 3.89161 | -0.88963 | -0.04531 |
| C | 3.92515 | 0.50439 | -0.01881 |
| H | 2.78056 | 2.33361 | 0.03254 |
| H | 4.81784 | -1.45138 | -0.06942 |
| H | 4.88094 | 1.01613 | -0.02303 |
| C | 0.06475 | -1.31299 | 0.00664 |
| H | -0.19781 | -1.90316 | -0.87556 |
| H | -0.15083 | -1.91007 | 0.89694 |
| N | -0.67205 | -0.05547 | 0.03047 |
| C | 0.15787 | 1.04719 | 0.04134 |
| C | -1.98701 | 0.33549 | 0.01570 |
| C | -0.63175 | 2.18072 | 0.04132 |
| C | -1.97404 | 1.72659 | 0.02375 |
| H | -2.87361 | 2.32114 | 0.01379 |
| H | -0.28332 | 3.20213 | 0.04710 |
| C | -3.21504 | -0.53492 | -0.01937 |
| C | -3.06975 | -1.90053 | 0.11270 |
| H | -2.12065 | -2.38667 | 0.27177 |
| H | -3.95880 | -2.52041 | 0.09539 |
| O | -4.30755 | 0.09998 | -0.16883 |
| H | 2.64008 | -2.64990 | -0.06167 |

## 7. Radical Cyclisation of 15

### 7.1 DMSO (Scheme S3.1)




37 38

**SM: 37** cyclisation to **38**

30

-709.3095148

| | | | |
|---|---|---|---|
| C | 4.58104 | -0.24887 | 0.06626 |
| C | 3.57387 | -0.58111 | -0.83645 |
| C | 2.21899 | -0.46079 | -0.49229 |
| C | 1.97671 | -0.00355 | 0.78379 |
| C | 2.92485 | 0.34277 | 1.71871 |
| C | 4.26559 | 0.21217 | 1.34390 |
| C | 1.12087 | -0.82697 | -1.48381 |
| C | -0.36685 | 1.42481 | -0.78481 |
| C | -0.87213 | 0.07126 | -0.58955 |
| C | -2.21732 | 0.00434 | -0.00811 |
| C | -2.91854 | 1.20227 | 0.25562 |
| C | -2.40637 | 2.45979 | 0.01924 |
| C | -1.09916 | 2.54725 | -0.50411 |
| H | 1.42590 | -1.77035 | -1.94943 |
| H | 5.61919 | -0.35412 | -0.22673 |
| H | 3.83453 | -0.94338 | -1.82747 |
| H | 2.65394 | 0.70083 | 2.70582 |
| H | 5.05238 | 0.46664 | 2.04502 |
| H | -3.91559 | 1.13775 | 0.67350 |
| H | -2.98186 | 3.34884 | 0.24365 |
| H | -0.65535 | 3.52326 | -0.68079 |
| C | -2.88338 | -1.25560 | 0.32630 |
| C | -4.30753 | -1.20848 | 0.88485 |
| H | -4.34957 | -0.67120 | 1.83468 |
| H | -4.99809 | -0.71910 | 0.19502 |
| H | -4.63309 | -2.23448 | 1.04560 |
| O | -2.37893 | -2.37015 | 0.19849 |
| N | -0.19231 | -1.01092 | -0.91213 |
| H | 1.14369 | -0.07879 | -2.29519 |
| H | 0.63770 | 1.55601 | -1.16388 |

**TS: 37** cyclisation to **38**

30

-709.3041328

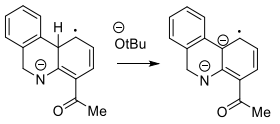
| | | | |
|---|---|---|---|
| C | 4.19763 | -0.64349 | 0.80006 |
| C | 3.28584 | -1.32197 | -0.01074 |
| C | 2.08972 | -0.71053 | -0.40197 |
| C | 1.85085 | 0.57069 | 0.05780 |
| C | 2.73377 | 1.27836 | 0.84772 |
| C | 3.92834 | 0.65315 | 1.23043 |
| C | 1.07338 | -1.42647 | -1.28808 |
| C | -0.15018 | 1.04407 | -1.18393 |
| C | -0.80525 | -0.16226 | -0.66975 |
| C | -2.07616 | 0.07380 | 0.02016 |
| C | -2.48675 | 1.39350 | 0.27573 |
| C | -1.80537 | 2.51034 | -0.18632 |
| C | -0.66445 | 2.31340 | -0.97363 |
| H | 1.36561 | -2.47703 | -1.36303 |
| H | 5.11942 | -1.13110 | 1.09659 |
| H | 3.50648 | -2.33328 | -0.34241 |
| H | 2.51917 | 2.29144 | 1.17643 |
| H | 4.63912 | 1.17743 | 1.86072 |
| H | -3.40477 | 1.55566 | 0.82781 |
| H | -2.18289 | 3.50581 | 0.01157 |
| H | -0.16276 | 3.16419 | -1.42482 |
| C | -2.95718 | -1.01591 | 0.44702 |
| C | -4.08621 | -0.70102 | 1.42614 |
| H | -3.74539 | -0.10841 | 2.27601 |
| H | -4.88427 | -0.14404 | 0.92813 |
| H | -4.49551 | -1.64545 | 1.78081 |
| O | -2.86259 | -2.17473 | 0.05055 |
| N | -0.27409 | -1.35800 | -0.76213 |
| H | 1.15689 | -1.01177 | -2.30684 |
| H | 0.62029 | 0.92654 | -1.93432 |

**Prod: 38** cyclised

30

-709.3701967

| | | | |
|---|---|---|---|
| C | -4.04103 | -0.48513 | -0.88523 |
| C | -3.20372 | -1.37654 | -0.21558 |
| C | -2.01500 | -0.92168 | 0.34469 |
| C | -1.64738 | 0.42052 | 0.22750 |
| C | -2.47464 | 1.30641 | -0.45674 |
| C | -3.67380 | 0.85225 | -1.00717 |
| C | -1.01094 | -1.79428 | 1.04544 |
| C | -0.32055 | 0.77450 | 0.87742 |
| C | 0.70707 | -0.30969 | 0.46468 |
| C | 2.02482 | 0.11977 | -0.00425 |
| C | 2.30288 | 1.51852 | -0.06575 |
| C | 1.36657 | 2.50738 | 0.28221 |
| C | 0.10672 | 2.19800 | 0.71406 |
| H | -1.25009 | -2.85015 | 0.90623 |
| H | -4.97119 | -0.83548 | -1.31794 |
| H | -3.47397 | -2.42462 | -0.13281 |
| H | -2.18644 | 2.34541 | -0.56756 |
| H | -4.31801 | 1.54417 | -1.53775 |
| H | 3.27374 | 1.84982 | -0.40641 |
| H | 1.66225 | 3.54939 | 0.20267 |
| H | -0.59269 | 2.97435 | 1.00371 |
| C | 3.04320 | -0.81538 | -0.41563 |
| C | 4.39085 | -0.24886 | -0.86807 |
| H | 4.28464 | 0.39822 | -1.74255 |
| H | 4.86650 | 0.34129 | -0.08070 |
| H | 5.03830 | -1.08591 | -1.12429 |
| O | 2.92731 | -2.05396 | -0.44084 |
| N | 0.35208 | -1.54778 | 0.57353 |
| H | -1.06452 | -1.59373 | 2.12848 |
| H | -0.48168 | 0.57862 | 1.95550 |




**38** **39**

**SM: 38** + tert-butoxide anion

44

-942.4969340

| | | | |
|---|---|---|---|
| C | 4.69901 | 0.32158 | -0.38556 |
| C | 3.67732 | 0.35918 | -1.33412 |
| C | 2.35082 | 0.25457 | -0.92980 |
| C | 2.02994 | 0.09139 | 0.42039 |
| C | 3.05361 | 0.03561 | 1.36370 |
| C | 4.38427 | 0.15843 | 0.96050 |
| C | 1.17144 | 0.24851 | -1.86030 |
| C | 0.54593 | -0.01987 | 0.71906 |
| C | -0.08318 | -0.98282 | -0.31339 |
| C | -1.03731 | -1.99217 | 0.15806 |
| C | -1.30147 | -2.07116 | 1.56049 |
| C | -0.68016 | -1.24265 | 2.51166 |
| C | 0.22052 | -0.27837 | 2.15461 |
| H | 1.49604 | 0.16106 | -2.89935 |
| H | 5.73365 | 0.40984 | -0.69686 |
| H | 3.91222 | 0.46924 | -2.38848 |
| H | 2.82137 | -0.11033 | 2.41226 |
| H | 5.17601 | 0.11745 | 1.70025 |
| H | -2.00004 | -2.81104 | 1.92638 |
| H | -0.93436 | -1.37734 | 3.55927 |
| H | 0.65675 | 0.37856 | 2.89972 |
| C | -1.71032 | -2.90058 | -0.73337 |
| C | -2.70071 | -3.89547 | -0.12096 |
| H | -2.21240 | -4.56772 | 0.58961 |
| H | -3.50828 | -3.38814 | 0.41333 |
| H | -3.12782 | -4.48670 | -0.92957 |
| O | -1.56445 | -2.95953 | -1.97113 |
| N | 0.23757 | -0.83775 | -1.55699 |
| H | 0.64372 | 1.20995 | -1.75478 |
| H | 0.12352 | 0.97684 | 0.44612 |
| O | -0.65130 | 3.01185 | 0.28832 |
| C | -1.96551 | 2.80430 | -0.05644 |
| C | -2.74466 | 4.13726 | -0.13675 |
| H | -2.28113 | 4.78974 | -0.88409 |
| H | -3.79796 | 3.99592 | -0.40670 |
| H | -2.70216 | 4.64670 | 0.83135 |
| C | -2.67956 | 1.90035 | 0.97654 |
| H | -2.15790 | 0.93975 | 1.04496 |
| H | -2.64616 | 2.37421 | 1.96390 |
| H | -3.72908 | 1.71246 | 0.72000 |
| C | -2.08186 | 2.10647 | -1.43154 |
| H | -1.58265 | 2.71270 | -2.19520 |
| H | -1.58542 | 1.13207 | -1.38907 |
| H | -3.12360 | 1.95308 | -1.73837 |

**TS: 38** + tert-butoxide anion

44

-942.4919052

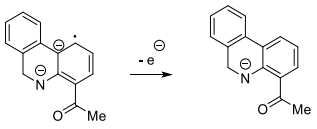
| | | | |
|---|---|---|---|
| C | 4.64152 | -0.75862 | -0.39032 |
| C | 3.63516 | -0.60535 | -1.34555 |
| C | 2.31639 | -0.41182 | -0.95126 |
| C | 1.96251 | -0.40438 | 0.40566 |
| C | 2.97568 | -0.58029 | 1.35611 |
| C | 4.30354 | -0.74321 | 0.96001 |
| C | 1.17312 | -0.20353 | -1.90120 |
| C | 0.51175 | -0.19761 | 0.71550 |
| C | -0.36560 | -0.92246 | -0.29114 |
| C | -1.62453 | -1.52882 | 0.18652 |
| C | -1.88430 | -1.52253 | 1.59535 |
| C | -1.01495 | -0.94285 | 2.53233 |
| C | 0.14949 | -0.33222 | 2.14371 |
| H | 1.46905 | -0.45790 | -2.92273 |
| H | 5.67252 | -0.89271 | -0.69711 |
| H | 3.87943 | -0.62467 | -2.40404 |
| H | 2.73458 | -0.60015 | 2.41236 |
| H | 5.07436 | -0.87070 | 1.71273 |
| H | -2.79218 | -1.97597 | 1.96923 |
| H | -1.28570 | -0.97162 | 3.58456 |
| H | 0.78166 | 0.15150 | 2.88148 |
| C | -2.61164 | -2.08008 | -0.69549 |
| C | -3.88888 | -2.64827 | -0.06437 |
| H | -3.67604 | -3.46828 | 0.62728 |
| H | -4.43968 | -1.88756 | 0.49619 |
| H | -4.52316 | -3.02163 | -0.86719 |
| O | -2.55295 | -2.13896 | -1.94734 |
| N | -0.01742 | -0.97140 | -1.54021 |
| H | 0.91183 | 0.86601 | -1.88275 |
| H | 0.34817 | 1.02165 | 0.44051 |
| O | 0.28188 | 2.45418 | 0.21862 |
| C | -1.00262 | 2.88846 | -0.08606 |
| C | -1.05724 | 4.42466 | -0.04095 |
| H | -0.34840 | 4.84193 | -0.76294 |
| H | -2.05660 | 4.80915 | -0.27380 |
| H | -0.77468 | 4.77454 | 0.95657 |
| C | -2.02578 | 2.33050 | 0.92326 |
| H | -1.99784 | 1.23641 | 0.91893 |
| H | -1.77342 | 2.67232 | 1.93255 |
| H | -3.04541 | 2.65892 | 0.69237 |
| C | -1.41708 | 2.42293 | -1.49565 |
| H | -0.71784 | 2.82253 | -2.23739 |
| H | -1.38216 | 1.33040 | -1.54637 |
| H | -2.42715 | 2.75673 | -1.75801 |

**Prod: 39** + tert-butanol

44

-942.5251437

| | | | |
|---|---|---|---|
| C | 4.76189 | -0.43530 | -0.35936 |
| C | 3.73286 | -0.43840 | -1.30991 |
| C | 2.40407 | -0.38475 | -0.91929 |
| C | 2.03944 | -0.38239 | 0.44847 |
| C | 3.08992 | -0.38838 | 1.39751 |
| C | 4.42146 | -0.40058 | 0.99373 |
| C | 1.24697 | -0.24310 | -1.86327 |
| C | 0.63131 | -0.46252 | 0.78013 |
| C | -0.24673 | -1.03204 | -0.24466 |
| C | -1.54282 | -1.59081 | 0.21639 |
| C | -1.89770 | -1.39166 | 1.59892 |
| C | -1.06448 | -0.76210 | 2.51696 |
| C | 0.19474 | -0.31727 | 2.13227 |
| H | 1.56026 | -0.45880 | -2.89028 |
| H | 5.80061 | -0.45149 | -0.66870 |
| H | 3.97209 | -0.45111 | -2.37050 |
| H | 2.86243 | -0.40707 | 2.45730 |
| H | 5.20434 | -0.40009 | 1.74592 |
| H | -2.85767 | -1.74486 | 1.95177 |
| H | -1.40414 | -0.62200 | 3.53940 |
| H | 0.84960 | 0.15292 | 2.85890 |
| C | -2.46449 | -2.28297 | -0.62847 |
| C | -3.81792 | -2.68201 | -0.02528 |
| H | -3.70818 | -3.41439 | 0.78194 |
| H | -4.36144 | -1.82825 | 0.39112 |
| H | -4.41830 | -3.13006 | -0.81681 |
| O | -2.29195 | -2.63301 | -1.83369 |
| N | 0.10102 | -1.07316 | -1.51971 |
| H | 0.93940 | 0.82202 | -1.84088 |
| H | 0.16303 | 1.67579 | 0.37362 |
| O | 0.03903 | 2.63386 | 0.24718 |
| C | -1.30670 | 2.85768 | -0.19104 |
| C | -1.46584 | 4.36916 | -0.28665 |
| H | -0.74435 | 4.78180 | -0.99626 |
| H | -2.47220 | 4.62569 | -0.62539 |
| H | -1.29885 | 4.83077 | 0.68971 |
| C | -2.27835 | 2.26912 | 0.82951 |
| H | -2.11632 | 1.19072 | 0.92658 |
| H | -2.12360 | 2.73201 | 1.80828 |
| H | -3.31305 | 2.44366 | 0.52143 |
| C | -1.52101 | 2.20390 | -1.55621 |
| H | -0.81909 | 2.61619 | -2.28619 |
| H | -1.35890 | 1.12348 | -1.48801 |
| H | -2.53916 | 2.38496 | -1.91161 |




39 40

**SM (Before SET): 39**

29

-708.8734067

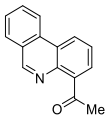
| | | | |
|---|---|---|---|
| C | -4.25019 | -0.50109 | -0.57560 |
| C | -3.28984 | -1.37406 | -0.04735 |
| C | -2.03226 | -0.91300 | 0.30985 |
| C | -1.65769 | 0.43701 | 0.10194 |
| C | -2.63749 | 1.30690 | -0.43517 |
| C | -3.90896 | 0.84192 | -0.75336 |
| C | -0.98802 | -1.72824 | 1.01218 |
| C | -0.28641 | 0.80680 | 0.36872 |
| C | 0.69342 | -0.27642 | 0.30560 |
| C | 2.09655 | 0.10945 | 0.01646 |
| C | 2.43155 | 1.50319 | 0.17155 |
| C | 1.47564 | 2.49599 | 0.37116 |
| C | 0.12235 | 2.16991 | 0.41137 |
| H | -1.24941 | -2.79133 | 0.99673 |
| H | -5.24052 | -0.85829 | -0.83280 |
| H | -3.53739 | -2.41967 | 0.11863 |
| H | -2.39061 | 2.34569 | -0.62618 |
| H | -4.63995 | 1.53288 | -1.16227 |
| H | 3.46815 | 1.80687 | 0.09985 |
| H | 1.79236 | 3.52991 | 0.47533 |
| H | -0.62479 | 2.95048 | 0.51771 |
| C | 3.11218 | -0.80830 | -0.38136 |
| C | 4.53502 | -0.26116 | -0.54886 |
| H | 4.59473 | 0.50848 | -1.32579 |
| H | 4.92091 | 0.18794 | 0.37245 |
| H | 5.18400 | -1.08997 | -0.83124 |
| O | 2.97164 | -2.04346 | -0.64101 |
| N | 0.34951 | -1.54255 | 0.46931 |
| H | -0.99236 | -1.41083 | 2.07774 |

**Prod (After SET): 40**

29

-708.8121885

| | | | |
|---|---|---|---|
| C | -4.27740 | -0.48206 | -0.48141 |
| C | -3.31826 | -1.35696 | 0.02321 |
| C | -2.03386 | -0.90577 | 0.31439 |
| C | -1.67921 | 0.42860 | 0.07110 |
| C | -2.64292 | 1.29580 | -0.46384 |
| C | -3.93422 | 0.84900 | -0.71907 |
| C | -0.97064 | -1.76748 | 0.93928 |
| C | -0.27772 | 0.80783 | 0.30006 |
| C | 0.70708 | -0.28460 | 0.25128 |
| C | 2.08607 | 0.14186 | -0.00175 |
| C | 2.41437 | 1.50193 | 0.14408 |
| C | 1.47759 | 2.48844 | 0.39558 |
| C | 0.12092 | 2.12167 | 0.41638 |
| H | -1.22844 | -2.82367 | 0.82168 |
| H | -5.28018 | -0.83416 | -0.69400 |
| H | -3.57213 | -2.39644 | 0.20886 |
| H | -2.37869 | 2.32029 | -0.70195 |
| H | -4.66917 | 1.53461 | -1.12577 |
| H | 3.45019 | 1.80277 | 0.04156 |
| H | 1.77601 | 3.52202 | 0.51334 |
| H | -0.63507 | 2.89690 | 0.50715 |
| C | 3.14571 | -0.79127 | -0.38291 |
| C | 4.58982 | -0.29318 | -0.40224 |
| H | 4.73897 | 0.45334 | -1.18596 |
| H | 4.87817 | 0.15992 | 0.54785 |
| H | 5.23437 | -1.14623 | -0.60642 |
| O | 2.94975 | -1.95810 | -0.71670 |
| N | 0.37398 | -1.54002 | 0.42222 |
| H | -0.97391 | -1.56715 | 2.02691 |



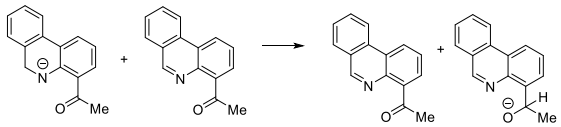
16

**Prod: 16**

28

-708.1155762

| | | | |
|---|---|---|---|
| C | 3.25938 | -0.63601 | -0.06414 |
| O | 4.24665 | -0.34068 | -0.70712 |
| C | 2.09626 | 0.31820 | -0.03538 |
| C | 0.74366 | -0.10641 | -0.03377 |
| C | 2.39464 | 1.66699 | 0.00542 |
| C | -0.28957 | 0.85812 | 0.03705 |
| C | 1.37277 | 2.62190 | 0.08735 |
| H | 3.43308 | 1.97619 | -0.01018 |
| C | -1.66469 | 0.39133 | 0.01802 |
| C | 0.05468 | 2.22283 | 0.10721 |
| C | -0.73377 | -1.86157 | -0.17069 |
| H | 1.62086 | 3.67501 | 0.13614 |
| C | -1.87838 | -0.99705 | -0.08649 |
| C | -2.79075 | 1.23667 | 0.09302 |
| H | -0.72183 | 2.97435 | 0.17003 |
| H | -0.90814 | -2.93257 | -0.26350 |
| C | -3.18383 | -1.52491 | -0.11479 |
| C | -4.06322 | 0.70617 | 0.06606 |
| H | -2.66944 | 2.30884 | 0.17371 |
| C | -4.26810 | -0.68165 | -0.03855 |
| H | -3.31751 | -2.59820 | -0.19716 |
| H | -4.91838 | 1.36904 | 0.12506 |
| H | -5.27526 | -1.07911 | -0.05924 |
| C | 3.22756 | -1.89618 | 0.76159 |
| H | 2.56791 | -1.80042 | 1.62290 |
| H | 2.84347 | -2.70938 | 0.14365 |
| H | 4.24583 | -2.12973 | 1.07199 |
| N | 0.49520 | -1.46273 | -0.14969 |



40 16 16 S33

**SM:** Hydride transfer between **40** and **16**

57

-1416.9443788

| | | | |
|---|---|---|---|
| C | 4.09971 | 0.25057 | -2.25134 |
| C | 3.53712 | 1.22362 | -1.43258 |
| C | 2.16249 | 1.26594 | -1.20146 |
| C | 1.31106 | 0.34678 | -1.83123 |
| C | 1.89111 | -0.62327 | -2.66530 |
| C | 3.26374 | -0.68169 | -2.86323 |
| C | 1.57702 | 2.27570 | -0.24522 |
| C | -0.14378 | 0.49252 | -1.63953 |
| C | -0.61656 | 1.68015 | -0.91795 |
| C | -2.06549 | 1.82659 | -0.82784 |
| C | -2.91246 | 0.92820 | -1.49894 |
| C | -2.43408 | -0.16577 | -2.18628 |
| C | -1.04273 | -0.36735 | -2.23166 |
| H | 2.17075 | 3.19652 | -0.29248 |
| H | 5.17049 | 0.22398 | -2.41738 |
| H | 4.17392 | 1.97029 | -0.96591 |
| H | 1.26734 | -1.34511 | -3.17795 |
| H | 3.68035 | -1.44839 | -3.50701 |
| H | -3.98148 | 1.08693 | -1.40527 |
| H | -3.10907 | -0.88226 | -2.63750 |
| H | -0.67466 | -1.24261 | -2.75783 |
| C | -2.73418 | 2.80244 | 0.03771 |
| C | -2.00088 | 3.46876 | 1.18292 |
| H | -2.74020 | 3.72141 | 1.94559 |
| H | -1.20646 | 2.83894 | 1.57834 |
| H | -1.52536 | 4.38670 | 0.83015 |
| O | -3.93949 | 3.05488 | -0.08810 |
| N | 0.17659 | 2.59847 | -0.41586 |
| H | 1.72458 | 1.89194 | 0.78304 |
| C | 2.58689 | 0.21800 | 2.62530 |
| O | 2.07597 | 0.42942 | 3.70393 |
| C | 1.99088 | -0.75100 | 1.64583 |
| C | 0.58422 | -0.87884 | 1.46711 |
| C | 2.85033 | -1.58543 | 0.95543 |
| C | 0.08560 | -1.92897 | 0.65910 |
| C | 2.35309 | -2.60442 | 0.13283 |
| H | 3.92224 | -1.46716 | 1.06391 |
| C | -1.35264 | -2.07338 | 0.52686 |
| C | 0.99481 | -2.78174 | 0.00340 |
| C | -1.51646 | -0.03836 | 1.86080 |
| H | 3.03969 | -3.25162 | -0.39883 |
| C | -2.16080 | -1.10215 | 1.14316 |
| C | -1.98399 | -3.12321 | -0.17224 |
| H | 0.62755 | -3.57590 | -0.63455 |
| H | -2.14949 | 0.73368 | 2.29763 |
| C | -3.56401 | -1.17299 | 1.05598 |
| C | -3.35944 | -3.19145 | -0.23519 |
| H | -1.39742 | -3.89332 | -0.65668 |
| C | -4.16067 | -2.21162 | 0.37887 |
| H | -4.16054 | -0.39909 | 1.52982 |
| H | -3.83029 | -4.01085 | -0.76626 |
| H | -5.24012 | -2.27570 | 0.31198 |
| C | 3.90612 | 0.86331 | 2.25857 |
| H | 4.72183 | 0.19117 | 2.54145 |
| H | 3.98283 | 1.05425 | 1.18839 |
| H | 4.01569 | 1.78684 | 2.82498 |
| N | -0.24085 | 0.06858 | 2.04336 |

**TS:** Hydride transfer between **40** and **16**

57

-1416.9054801

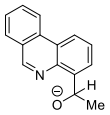
| | | | |
|---|---|---|---|
| C | -4.00974 | -0.45497 | 2.21452 |
| C | -3.61584 | 0.63311 | 1.45657 |
| C | -2.25917 | 0.87423 | 1.20634 |
| C | -1.27416 | 0.04718 | 1.77078 |
| C | -1.69193 | -1.05978 | 2.53163 |
| C | -3.03627 | -1.31525 | 2.73600 |
| C | -1.82956 | 1.98574 | 0.34058 |
| C | 0.12643 | 0.43817 | 1.59910 |
| C | 0.39237 | 1.67847 | 0.93673 |
| C | 1.75077 | 2.11455 | 0.88006 |
| C | 2.76291 | 1.36967 | 1.47640 |
| C | 2.49238 | 0.15111 | 2.09249 |
| C | 1.18179 | -0.30267 | 2.13741 |
| H | -2.60113 | 2.73371 | 0.14106 |
| H | -5.06039 | -0.63931 | 2.40514 |
| H | -4.35640 | 1.31534 | 1.05209 |
| H | -0.96239 | -1.72495 | 2.97634 |
| H | -3.33418 | -2.17675 | 3.32288 |
| H | 3.78081 | 1.73788 | 1.41030 |
| H | 3.29345 | -0.44568 | 2.51088 |
| H | 0.97981 | -1.25502 | 2.61417 |
| C | 2.18168 | 3.32583 | 0.12274 |
| C | 1.51980 | 3.67309 | -1.18863 |
| H | 2.28329 | 4.07907 | -1.85435 |
| H | 1.01915 | 2.81088 | -1.62694 |
| H | 0.76147 | 4.43816 | -1.01279 |
| O | 3.13066 | 3.98765 | 0.51431 |
| N | -0.57262 | 2.47636 | 0.40942 |
| H | -2.00543 | 1.38984 | -0.94535 |
| C | -2.33224 | 0.77681 | -2.09406 |
| O | -1.79839 | 1.36041 | -3.10458 |
| C | -1.79248 | -0.57556 | -1.62923 |
| C | -0.39190 | -0.80255 | -1.46889 |
| C | -2.66522 | -1.58833 | -1.27110 |
| C | 0.07053 | -2.03139 | -0.93009 |
| C | -2.20674 | -2.81595 | -0.77022 |
| H | -3.73265 | -1.44264 | -1.37569 |
| C | 1.49552 | -2.19896 | -0.70567 |
| C | -0.86096 | -3.03392 | -0.59534 |
| C | 1.74347 | 0.05020 | -1.60526 |
| H | -2.92076 | -3.58859 | -0.50866 |
| C | 2.34255 | -1.13338 | -1.05890 |
| C | 2.07959 | -3.34874 | -0.13037 |
| H | -0.52353 | -3.97945 | -0.19081 |
| H | 2.40477 | 0.87605 | -1.87129 |
| C | 3.73227 | -1.21361 | -0.84906 |
| C | 3.44175 | -3.41445 | 0.07355 |
| H | 1.46595 | -4.19090 | 0.16234 |
| C | 4.28080 | -2.34361 | -0.28833 |
| H | 4.35484 | -0.36852 | -1.12491 |
| H | 3.87219 | -4.30405 | 0.51865 |
| H | 5.34855 | -2.41174 | -0.11855 |
| C | -3.85627 | 0.93515 | -1.99638 |
| H | -4.32972 | 0.36694 | -2.80455 |
| H | -4.28203 | 0.60963 | -1.04822 |
| H | -4.08729 | 1.99100 | -2.14691 |
| N | 0.47840 | 0.21985 | -1.79842 |

**Prod:** Hydride transfer results in **16** and **S33**

57

-1416.9488832

| | | | |
|---|---|---|---|
| C | 2.25520 | -2.85565 | -2.41522 |
| C | 2.22552 | -1.47987 | -2.43298 |
| C | 1.05134 | -0.79594 | -2.06654 |
| C | -0.10567 | -1.50413 | -1.68867 |
| C | -0.04911 | -2.91244 | -1.66131 |
| C | 1.11054 | -3.56944 | -2.01812 |
| C | 1.00074 | 0.63925 | -2.07397 |
| C | -1.28305 | -0.72865 | -1.34617 |
| C | -1.19263 | 0.68340 | -1.39061 |
| C | -2.33816 | 1.46459 | -1.08320 |
| C | -3.52766 | 0.83883 | -0.75743 |
| C | -3.61119 | -0.55768 | -0.69737 |
| C | -2.50543 | -1.32637 | -0.98110 |
| H | 1.90182 | 1.18020 | -2.35861 |
| H | 3.15590 | -3.38991 | -2.69239 |
| H | 3.10162 | -0.90620 | -2.71744 |
| H | -0.91260 | -3.49280 | -1.36196 |
| H | 1.13866 | -4.65267 | -1.99251 |
| H | -4.39473 | 1.44833 | -0.53170 |
| H | -4.54258 | -1.03162 | -0.41212 |
| H | -2.58265 | -2.40435 | -0.91943 |
| C | -2.34907 | 2.96986 | -1.07957 |
| C | -1.15676 | 3.74524 | -0.58762 |
| H | -1.50799 | 4.69904 | -0.19335 |
| H | -0.58905 | 3.18726 | 0.15748 |
| H | -0.48562 | 3.92552 | -1.42969 |
| O | -3.36334 | 3.54824 | -1.42175 |
| N | -0.03949 | 1.34448 | -1.77110 |
| H | 2.50360 | 2.79620 | 1.98635 |
| C | 3.11098 | 2.34371 | 1.17588 |
| O | 4.45201 | 2.47566 | 1.38855 |
| C | 2.64390 | 0.87381 | 1.11157 |
| C | 1.30664 | 0.47302 | 1.39242 |
| C | 3.56484 | -0.10710 | 0.80193 |
| C | 0.95259 | -0.90080 | 1.39635 |
| C | 3.21126 | -1.46534 | 0.76133 |
| H | 4.58451 | 0.20919 | 0.61442 |
| C | -0.40402 | -1.26650 | 1.75958 |
| C | 1.92874 | -1.86137 | 1.06324 |
| C | -0.82334 | 1.12577 | 1.99951 |
| H | 3.95462 | -2.20982 | 0.49639 |
| C | -1.29866 | -0.22813 | 2.08331 |
| C | -0.87984 | -2.59435 | 1.81211 |
| H | 1.67410 | -2.91309 | 1.03634 |
| H | -1.53107 | 1.92734 | 2.21675 |
| C | -2.62038 | -0.51172 | 2.47696 |
| C | -2.17807 | -2.85769 | 2.19707 |
| H | -0.22887 | -3.42034 | 1.55549 |
| C | -3.05724 | -1.81518 | 2.54135 |
| H | -3.28526 | 0.31149 | 2.71827 |
| H | -2.52548 | -3.88391 | 2.23558 |
| H | -4.07340 | -2.04087 | 2.84183 |
| C | 2.65660 | 3.03878 | -0.12833 |
| H | 3.24457 | 2.63467 | -0.96036 |
| H | 1.59532 | 2.89105 | -0.34250 |
| H | 2.86655 | 4.11045 | -0.05494 |
| N | 0.38193 | 1.46785 | 1.68357 |




S33

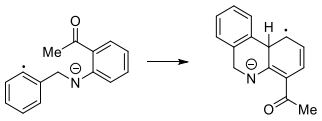
**Prod: S33**

29

-708.8113747

| | | | |
|---|---|---|---|
| H | 2.84092 | -1.57502 | -0.97048 |
| C | 3.20989 | -0.80983 | -0.25665 |
| O | 4.39887 | -0.26364 | -0.63469 |
| C | 2.06554 | 0.21834 | -0.15296 |
| C | 0.69323 | -0.15777 | -0.12722 |
| C | 2.37601 | 1.56079 | -0.06838 |
| C | -0.32181 | 0.82525 | -0.00289 |
| C | 1.37779 | 2.53996 | 0.06337 |
| H | 3.42461 | 1.83068 | -0.11543 |
| C | -1.70773 | 0.39013 | 0.01215 |
| C | 0.04839 | 2.18200 | 0.09796 |
| C | -0.84045 | -1.88065 | -0.22892 |
| H | 1.65321 | 3.58664 | 0.13466 |
| C | -1.96217 | -0.99054 | -0.10160 |
| C | -2.81256 | 1.26077 | 0.13112 |
| H | -0.70802 | 2.94979 | 0.19891 |
| H | -1.04510 | -2.94675 | -0.32568 |
| C | -3.28169 | -1.48422 | -0.09817 |
| C | -4.09892 | 0.76469 | 0.13416 |
| H | -2.66174 | 2.32849 | 0.22040 |
| C | -4.34291 | -0.61650 | 0.01892 |
| H | -3.44426 | -2.55308 | -0.18959 |
| H | -4.93421 | 1.44910 | 0.22578 |
| H | -5.35996 | -0.98899 | 0.02230 |
| C | 3.30292 | -1.52324 | 1.11544 |
| H | 3.62206 | -0.79827 | 1.87223 |
| H | 2.35366 | -1.96776 | 1.42648 |
| H | 4.06065 | -2.31021 | 1.05697 |
| N | 0.39629 | -1.51008 | -0.24243 |

## 7.2 Benzene (Scheme S3.1)



37 38

**SM: 37** cyclisation to **38**

30

-709.2689329

| | | | |
|---|---|---|---|
| C | 4.58455 | -0.41627 | 0.14332 |
| C | 3.56161 | -0.80707 | -0.71828 |
| C | 2.22382 | -0.47117 | -0.46553 |
| C | 2.01126 | 0.25740 | 0.68414 |
| C | 2.97600 | 0.67465 | 1.57053 |
| C | 4.30037 | 0.32359 | 1.28946 |
| C | 1.11199 | -0.90267 | -1.41676 |
| C | -0.39707 | 1.38724 | -0.87493 |
| C | -0.87900 | 0.04138 | -0.58251 |
| C | -2.22095 | -0.00483 | 0.00959 |
| C | -2.92019 | 1.19687 | 0.23461 |
| C | -2.42144 | 2.44844 | -0.06902 |
| C | -1.13195 | 2.51736 | -0.63361 |
| H | 1.41531 | -1.87429 | -1.82198 |
| H | 5.60840 | -0.69720 | -0.07698 |
| H | 3.79663 | -1.39249 | -1.60361 |
| H | 2.72610 | 1.25144 | 2.45441 |
| H | 5.09723 | 0.62295 | 1.96143 |
| H | -3.91043 | 1.14571 | 0.67111 |
| H | -2.99826 | 3.34343 | 0.12757 |
| H | -0.70257 | 3.48588 | -0.87702 |
| C | -2.88404 | -1.26087 | 0.37652 |
| C | -4.29203 | -1.19064 | 0.98660 |
| H | -4.30397 | -0.61369 | 1.91393 |
| H | -5.00744 | -0.73463 | 0.29827 |
| H | -4.60277 | -2.21232 | 1.19796 |
| O | -2.40566 | -2.37855 | 0.23483 |
| N | -0.19018 | -1.05099 | -0.82292 |
| H | 1.12686 | -0.20591 | -2.27501 |
| H | 0.59392 | 1.50600 | -1.29302 |

**TS: 37** cyclisation to **38**

30

-709.2652784

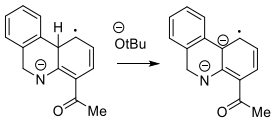
| | | | |
|---|---|---|---|
| C | 4.20852 | -0.67887 | 0.78337 |
| C | 3.27799 | -1.33006 | -0.02784 |
| C | 2.09422 | -0.69166 | -0.41190 |
| C | 1.88435 | 0.59254 | 0.05417 |
| C | 2.78669 | 1.27162 | 0.84717 |
| C | 3.96899 | 0.62008 | 1.22272 |
| C | 1.06265 | -1.39224 | -1.29540 |
| C | -0.17527 | 1.07814 | -1.17429 |
| C | -0.81141 | -0.13959 | -0.66575 |
| C | -2.08668 | 0.07612 | 0.02413 |
| C | -2.51205 | 1.38190 | 0.29336 |
| C | -1.84170 | 2.51531 | -0.15523 |
| C | -0.69986 | 2.33903 | -0.94294 |
| H | 1.35119 | -2.44318 | -1.38533 |
| H | 5.11921 | -1.19047 | 1.07499 |
| H | 3.47163 | -2.34582 | -0.36364 |
| H | 2.59213 | 2.28563 | 1.18593 |
| H | 4.69210 | 1.12390 | 1.85648 |
| H | -3.43344 | 1.52618 | 0.84597 |
| H | -2.22944 | 3.50434 | 0.05571 |
| H | -0.20496 | 3.20121 | -1.38084 |
| C | -2.95550 | -1.03668 | 0.43076 |
| C | -4.06144 | -0.75443 | 1.45233 |
| H | -3.70018 | -0.17767 | 2.30504 |
| H | -4.87970 | -0.19652 | 0.98889 |
| H | -4.44718 | -1.71405 | 1.79271 |
| O | -2.87367 | -2.17453 | -0.00710 |
| N | -0.27459 | -1.32839 | -0.75702 |
| H | 1.13913 | -0.96345 | -2.31009 |
| H | 0.60399 | 0.97767 | -1.91777 |

**Prod: 38** cyclised

30

-709.3311818

| | | | |
|---|---|---|---|
| C | -4.04792 | -0.48957 | -0.87668 |
| C | -3.19979 | -1.38281 | -0.22408 |
| C | -2.01073 | -0.92929 | 0.33589 |
| C | -1.65113 | 0.41672 | 0.23258 |
| C | -2.48824 | 1.30384 | -0.43724 |
| C | -3.68888 | 0.85095 | -0.98447 |
| C | -0.99613 | -1.80686 | 1.01487 |
| C | -0.32289 | 0.77351 | 0.87574 |
| C | 0.70914 | -0.30652 | 0.45345 |
| C | 2.02426 | 0.12978 | -0.00725 |
| C | 2.29648 | 1.52499 | -0.07389 |
| C | 1.35860 | 2.51071 | 0.27767 |
| C | 0.09998 | 2.19913 | 0.71482 |
| H | -1.22917 | -2.86192 | 0.85538 |
| H | -4.97790 | -0.84106 | -1.30966 |
| H | -3.45921 | -2.43504 | -0.15708 |
| H | -2.19908 | 2.34309 | -0.54273 |
| H | -4.33921 | 1.54564 | -1.50454 |
| H | 3.26694 | 1.85920 | -0.41356 |
| H | 1.65150 | 3.55400 | 0.19953 |
| H | -0.59714 | 2.97446 | 1.01400 |
| C | 3.04967 | -0.81401 | -0.40137 |
| C | 4.38633 | -0.24137 | -0.89102 |
| H | 4.25489 | 0.40623 | -1.76171 |
| H | 4.87935 | 0.34753 | -0.11274 |
| H | 5.02421 | -1.08152 | -1.16130 |
| O | 2.95153 | -2.04557 | -0.38037 |
| N | 0.36110 | -1.54596 | 0.54670 |
| H | -1.04978 | -1.62772 | 2.10264 |
| H | -0.47780 | 0.56827 | 1.95363 |




**38** **39**

**SM: 38** + tert-butoxide anion

44

-942.3803722

| | | | |
|---|---|---|---|
| C | -1.63032 | 3.69975 | 0.22487 |
| C | -1.16058 | 3.01134 | -0.89485 |
| C | -0.53728 | 1.77850 | -0.74466 |
| C | -0.36563 | 1.22824 | 0.53007 |
| C | -0.81278 | 1.92482 | 1.64726 |
| C | -1.45191 | 3.15671 | 1.49414 |
| C | 0.02095 | 0.94355 | -1.86244 |
| C | 0.29995 | -0.13326 | 0.53638 |
| C | 1.53640 | -0.04344 | -0.39139 |
| C | 2.82389 | -0.55963 | 0.09624 |
| C | 2.86751 | -1.13819 | 1.39757 |
| C | 1.74835 | -1.21432 | 2.24926 |
| C | 0.52183 | -0.72948 | 1.88823 |
| H | 0.04156 | 1.50708 | -2.79840 |
| H | -2.12500 | 4.65814 | 0.10637 |
| H | -1.28292 | 3.43389 | -1.88811 |
| H | -0.66849 | 1.50411 | 2.63661 |
| H | -1.80771 | 3.69213 | 2.36832 |
| H | 3.80239 | -1.53488 | 1.77070 |
| H | 1.87344 | -1.68000 | 3.22395 |
| H | -0.33414 | -0.83005 | 2.54826 |
| C | 4.03035 | -0.49074 | -0.68711 |
| C | 5.30529 | -1.09253 | -0.07248 |
| H | 5.58709 | -0.58418 | 0.85428 |
| H | 5.18221 | -2.15429 | 0.15908 |
| H | 6.10615 | -0.97476 | -0.80171 |
| O | 4.15650 | 0.01257 | -1.81584 |
| N | 1.37732 | 0.47702 | -1.55791 |
| H | -0.65690 | 0.08069 | -1.98073 |
| H | -0.42640 | -0.76195 | -0.02805 |
| O | -2.19314 | -1.44093 | -1.21230 |
| C | -3.24612 | -1.72356 | -0.40280 |
| C | -3.08700 | -3.11459 | 0.26757 |
| H | -3.00405 | -3.87942 | -0.51163 |
| H | -2.15989 | -3.12331 | 0.84982 |
| H | -3.92355 | -3.37435 | 0.93044 |
| C | -3.38764 | -0.67575 | 0.73238 |
| H | -2.47569 | -0.67196 | 1.33734 |
| H | -3.49325 | 0.32155 | 0.29231 |
| H | -4.24622 | -0.86876 | 1.39005 |
| C | -4.58175 | -1.73782 | -1.19350 |
| H | -4.51207 | -2.48171 | -1.99388 |
| H | -5.45409 | -1.97149 | -0.56811 |
| H | -4.73167 | -0.75635 | -1.65486 |

**TS: 38** + tert-butoxide anion

44

-942.3748136

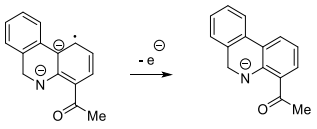
| | | | |
|---|---|---|---|
| C | -2.30341 | 3.61536 | 0.28038 |
| C | -1.58450 | 3.13522 | -0.81723 |
| C | -0.82797 | 1.97538 | -0.71222 |
| C | -0.73958 | 1.28428 | 0.50777 |
| C | -1.44220 | 1.78590 | 1.60902 |
| C | -2.22744 | 2.93286 | 1.49149 |
| C | -0.04487 | 1.36062 | -1.83673 |
| C | 0.09909 | 0.05309 | 0.50249 |
| C | 1.36294 | 0.28730 | -0.31885 |
| C | 2.63707 | -0.27307 | 0.17728 |
| C | 2.61106 | -1.02571 | 1.39175 |
| C | 1.45429 | -1.18907 | 2.17130 |
| C | 0.25563 | -0.63312 | 1.80231 |
| H | 0.03488 | 2.05766 | -2.67658 |
| H | -2.90800 | 4.51185 | 0.19197 |
| H | -1.62158 | 3.66269 | -1.76689 |
| H | -1.36913 | 1.28352 | 2.56713 |
| H | -2.77218 | 3.30045 | 2.35577 |
| H | 3.52411 | -1.47767 | 1.75615 |
| H | 1.52066 | -1.76821 | 3.08948 |
| H | -0.62666 | -0.79097 | 2.41567 |
| C | 3.88674 | -0.09352 | -0.50704 |
| C | 5.12760 | -0.76579 | 0.10989 |
| H | 5.33854 | -0.38736 | 1.11504 |
| H | 5.00953 | -1.85098 | 0.18768 |
| H | 5.97506 | -0.54416 | -0.53842 |
| O | 4.09340 | 0.55653 | -1.55190 |
| N | 1.29693 | 0.94966 | -1.42763 |
| H | -0.59923 | 0.47086 | -2.17437 |
| H | -0.58822 | -0.72805 | -0.23267 |
| O | -1.36866 | -1.54707 | -1.10831 |
| C | -2.40775 | -2.22437 | -0.50704 |
| C | -1.88003 | -3.40598 | 0.33502 |
| H | -1.33967 | -4.10047 | -0.31574 |
| H | -1.17735 | -3.02668 | 1.08262 |
| H | -2.68439 | -3.95192 | 0.84424 |
| C | -3.22153 | -1.29028 | 0.41549 |
| H | -2.58476 | -0.91332 | 1.22019 |
| H | -3.57268 | -0.42736 | -0.15939 |
| H | -4.08620 | -1.79712 | 0.86152 |
| C | -3.35605 | -2.78072 | -1.58746 |
| H | -2.79253 | -3.43514 | -2.25920 |
| H | -4.19102 | -3.34861 | -1.15745 |
| H | -3.76011 | -1.95260 | -2.17741 |

**Prod: 39** + tert-butanol

44

-942.4058202

| | | | |
|---|---|---|---|
| C | 3.06303 | -3.28308 | 0.12012 |
| C | 2.14454 | -2.96762 | -0.89875 |
| C | 1.16474 | -2.01177 | -0.70661 |
| C | 1.00840 | -1.35495 | 0.54373 |
| C | 1.94229 | -1.68279 | 1.56444 |
| C | 2.94872 | -2.61720 | 1.34207 |
| C | 0.25918 | -1.49734 | -1.78788 |
| C | -0.09941 | -0.45674 | 0.70468 |
| C | -1.23984 | -0.65016 | -0.21621 |
| C | -2.54817 | -0.12280 | 0.23283 |
| C | -2.55221 | 0.77440 | 1.35688 |
| C | -1.42734 | 1.02382 | 2.13246 |
| C | -0.22197 | 0.37751 | 1.85291 |
| H | 0.26618 | -2.17472 | -2.64942 |
| H | 3.84598 | -4.01536 | -0.04361 |
| H | 2.22131 | -3.45391 | -1.86911 |
| H | 1.85407 | -1.22250 | 2.54252 |
| H | 3.64653 | -2.84313 | 2.14434 |
| H | -3.47625 | 1.26455 | 1.63669 |
| H | -1.49508 | 1.71222 | 2.97112 |
| H | 0.64023 | 0.53829 | 2.49385 |
| C | -3.78629 | -0.43675 | -0.41311 |
| C | -5.04588 | 0.29536 | 0.08745 |
| H | -5.27541 | 0.04661 | 1.12930 |
| H | -4.94348 | 1.38393 | 0.02922 |
| H | -5.87883 | -0.01917 | -0.54159 |
| O | -3.97866 | -1.26372 | -1.33471 |
| N | -1.11318 | -1.26744 | -1.36564 |
| H | 0.68782 | -0.53360 | -2.13403 |
| H | 0.30296 | 1.41135 | -0.53450 |
| O | 0.58900 | 2.15492 | -1.09528 |
| C | 1.73916 | 2.75579 | -0.51201 |
| C | 1.32589 | 3.57937 | 0.71027 |
| H | 0.61875 | 4.35769 | 0.41123 |
| H | 0.83607 | 2.93040 | 1.44075 |
| H | 2.19571 | 4.05182 | 1.17747 |
| C | 2.75249 | 1.68175 | -0.11444 |
| H | 2.33645 | 1.02903 | 0.65695 |
| H | 2.99898 | 1.05999 | -0.97992 |
| H | 3.67087 | 2.13939 | 0.26593 |
| C | 2.31922 | 3.66317 | -1.59220 |
| H | 1.56943 | 4.39299 | -1.90837 |
| H | 3.19633 | 4.19800 | -1.21782 |
| H | 2.61144 | 3.06879 | -2.46134 |




39 40

**SM (Before SET): 39**

29

-708.7533311

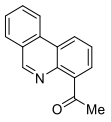
| | | | |
|---|---|---|---|
| C | -4.27121 | -0.50667 | -0.55120 |
| C | -3.28326 | -1.38655 | -0.06941 |
| C | -2.02582 | -0.92901 | 0.27578 |
| C | -1.65900 | 0.43470 | 0.10360 |
| C | -2.66776 | 1.31311 | -0.38461 |
| C | -3.93947 | 0.84473 | -0.69081 |
| C | -0.97241 | -1.76012 | 0.94704 |
| C | -0.29770 | 0.80613 | 0.35497 |
| C | 0.69892 | -0.27876 | 0.28799 |
| C | 2.09658 | 0.12158 | 0.00568 |
| C | 2.42286 | 1.51739 | 0.13445 |
| C | 1.46387 | 2.50229 | 0.34206 |
| C | 0.11049 | 2.16711 | 0.40238 |
| H | -1.21997 | -2.82588 | 0.87870 |
| H | -5.26398 | -0.86517 | -0.79965 |
| H | -3.51463 | -2.44071 | 0.07006 |
| H | -2.43286 | 2.35857 | -0.55248 |
| H | -4.68389 | 1.54357 | -1.06466 |
| H | 3.45603 | 1.82980 | 0.04696 |
| H | 1.77354 | 3.54026 | 0.43556 |
| H | -0.63771 | 2.94575 | 0.51983 |
| C | 3.12520 | -0.80376 | -0.35655 |
| C | 4.55154 | -0.24224 | -0.51535 |
| H | 4.61285 | 0.50736 | -1.31186 |
| H | 4.91518 | 0.23176 | 0.40289 |
| H | 5.20442 | -1.07852 | -0.76665 |
| O | 3.00884 | -2.03318 | -0.58460 |
| N | 0.37095 | -1.54101 | 0.43933 |
| H | -0.99329 | -1.49379 | 2.02679 |

**Prod (After SET): 40**

29

-708.7732472

| | | | |
|---|---|---|---|
| C | -4.27535 | -0.49062 | -0.47992 |
| C | -3.30930 | -1.36115 | 0.01972 |
| C | -2.02763 | -0.90668 | 0.31340 |
| C | -1.67818 | 0.43101 | 0.07256 |
| C | -2.64829 | 1.29291 | -0.45973 |
| C | -3.93828 | 0.84229 | -0.71327 |
| C | -0.96266 | -1.76717 | 0.93874 |
| C | -0.28045 | 0.81345 | 0.29878 |
| C | 0.70482 | -0.28096 | 0.25684 |
| C | 2.08414 | 0.14626 | -0.00217 |
| C | 2.41126 | 1.50188 | 0.13800 |
| C | 1.47401 | 2.49405 | 0.38683 |
| C | 0.11911 | 2.12804 | 0.40951 |
| H | -1.21429 | -2.82427 | 0.81091 |
| H | -5.27651 | -0.84781 | -0.69316 |
| H | -3.55544 | -2.40375 | 0.19972 |
| H | -2.38580 | 2.31746 | -0.69974 |
| H | -4.67638 | 1.52616 | -1.11831 |
| H | 3.44734 | 1.80228 | 0.03189 |
| H | 1.77464 | 3.52759 | 0.50094 |
| H | -0.63772 | 2.90302 | 0.50106 |
| C | 3.13947 | -0.79572 | -0.38585 |
| C | 4.59010 | -0.30030 | -0.38915 |
| H | 4.74988 | 0.44431 | -1.17300 |
| H | 4.86991 | 0.15124 | 0.56459 |
| H | 5.22859 | -1.15961 | -0.58713 |
| O | 2.94472 | -1.95290 | -0.73157 |
| N | 0.38253 | -1.53195 | 0.43725 |
| H | -0.97623 | -1.57345 | 2.02822 |



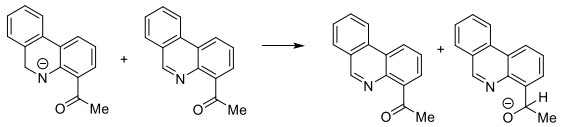
16

**Prod: 16**

28

-708.1103926

| | | | |
|---|---|---|---|
| C | 3.26851 | -0.63245 | -0.06342 |
| O | 4.26867 | -0.30225 | -0.66285 |
| C | 2.09594 | 0.31516 | -0.03000 |
| C | 0.74288 | -0.10817 | -0.02801 |
| C | 2.39238 | 1.66419 | 0.00818 |
| C | -0.29078 | 0.85706 | 0.03846 |
| C | 1.37129 | 2.61944 | 0.08655 |
| H | 3.43164 | 1.96982 | -0.01395 |
| C | -1.66599 | 0.39150 | 0.01836 |
| C | 0.05330 | 2.22131 | 0.10556 |
| C | -0.73684 | -1.86158 | -0.15963 |
| H | 1.61994 | 3.67269 | 0.13152 |
| C | -1.88158 | -0.99640 | -0.08218 |
| C | -2.79216 | 1.23734 | 0.08808 |
| H | -0.72357 | 2.97274 | 0.16441 |
| H | -0.91091 | -2.93331 | -0.24816 |
| C | -3.18752 | -1.52199 | -0.11173 |
| C | -4.06498 | 0.70922 | 0.05965 |
| H | -2.66928 | 2.30956 | 0.16537 |
| C | -4.27133 | -0.67834 | -0.04101 |
| H | -3.32200 | -2.59552 | -0.19090 |
| H | -4.91943 | 1.37348 | 0.11425 |
| H | -5.27881 | -1.07499 | -0.06302 |
| C | 3.22484 | -1.92829 | 0.70632 |
| H | 2.57701 | -1.85983 | 1.57963 |
| H | 2.81625 | -2.70632 | 0.06008 |
| H | 4.24369 | -2.18906 | 0.99131 |
| N | 0.49121 | -1.46417 | -0.13700 |



40 16 16 S33

**SM:** Hydride transfer between **40** and **16**

57

-1416.9065168

| | | | |
|---|---|---|---|
| C | 4.40909 | 1.35674 | -1.49923 |
| C | 3.76213 | 1.63235 | -0.29955 |
| C | 2.37217 | 1.58684 | -0.19783 |
| C | 1.59103 | 1.30597 | -1.32826 |
| C | 2.25616 | 1.06341 | -2.54218 |
| C | 3.64138 | 1.06735 | -2.62545 |
| C | 1.69213 | 1.79715 | 1.13196 |
| C | 0.12511 | 1.33007 | -1.19322 |
| C | -0.43269 | 1.82950 | 0.07492 |
| C | -1.89272 | 1.93133 | 0.11956 |
| C | -2.65428 | 1.60694 | -1.01388 |
| C | -2.09638 | 1.13974 | -2.18461 |
| C | -0.69952 | 1.00260 | -2.24588 |
| H | 2.26061 | 2.53910 | 1.70688 |
| H | 5.49122 | 1.38184 | -1.56127 |
| H | 4.34466 | 1.89209 | 0.58071 |
| H | 1.68723 | 0.87099 | -3.44321 |
| H | 4.12247 | 0.86213 | -3.57579 |
| H | -3.73053 | 1.70069 | -0.92266 |
| H | -2.71390 | 0.86867 | -3.03199 |
| H | -0.26375 | 0.61981 | -3.16376 |
| C | -2.67361 | 2.25174 | 1.32372 |
| C | -2.00174 | 2.60845 | 2.62977 |
| H | -2.77841 | 2.74187 | 3.38356 |
| H | -1.28848 | 1.83440 | 2.91779 |
| H | -1.40097 | 3.51235 | 2.51659 |
| O | -3.91016 | 2.21940 | 1.30981 |
| N | 0.30220 | 2.18321 | 1.10125 |
| H | 1.77792 | 0.85796 | 1.71311 |
| C | 2.46361 | -1.62500 | 2.29208 |
| O | 1.96397 | -2.13205 | 3.27209 |
| C | 1.80851 | -1.69478 | 0.94282 |
| C | 0.39784 | -1.58741 | 0.78970 |
| C | 2.60353 | -1.93672 | -0.16090 |
| C | -0.17932 | -1.86986 | -0.46985 |
| C | 2.03048 | -2.16240 | -1.42025 |
| H | 3.68182 | -1.96817 | -0.05463 |
| C | -1.62351 | -1.81191 | -0.59023 |
| C | 0.66252 | -2.15295 | -1.56331 |
| C | -1.61498 | -0.99147 | 1.70911 |
| H | 2.66758 | -2.33897 | -2.27832 |
| C | -2.34503 | -1.34671 | 0.52312 |
| C | -2.34121 | -2.19504 | -1.74159 |
| H | 0.23053 | -2.33202 | -2.54021 |
| H | -2.17690 | -0.57759 | 2.54628 |
| C | -3.74604 | -1.22380 | 0.46944 |
| C | -3.71565 | -2.10202 | -1.77063 |
| H | -1.81845 | -2.57771 | -2.60909 |
| C | -4.42658 | -1.60031 | -0.66594 |
| H | -4.27143 | -0.82169 | 1.32916 |
| H | -4.25385 | -2.40647 | -2.66112 |
| H | -5.50523 | -1.50812 | -0.71332 |
| C | 3.83424 | -0.98112 | 2.37535 |
| H | 4.59076 | -1.75209 | 2.19659 |
| H | 3.96789 | -0.19018 | 1.63853 |
| H | 3.97587 | -0.60009 | 3.38583 |
| N | -0.34038 | -1.13747 | 1.86626 |

**TS:** Hydride transfer between **40** and **16**

57

-1416.8637978

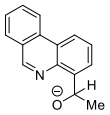
| | | | |
|---|---|---|---|
| C | -4.00972 | -0.55095 | 2.16211 |
| C | -3.61331 | 0.57575 | 1.46569 |
| C | -2.25549 | 0.84034 | 1.24728 |
| C | -1.27193 | -0.00671 | 1.78582 |
| C | -1.69295 | -1.15270 | 2.48455 |
| C | -3.03713 | -1.42823 | 2.65615 |
| C | -1.82435 | 1.99409 | 0.44644 |
| C | 0.12744 | 0.39208 | 1.63832 |
| C | 0.39447 | 1.64736 | 1.00727 |
| C | 1.75516 | 2.07173 | 0.92723 |
| C | 2.76701 | 1.30977 | 1.49760 |
| C | 2.49453 | 0.08643 | 2.10578 |
| C | 1.18371 | -0.36342 | 2.15496 |
| H | -2.59352 | 2.74532 | 0.25574 |
| H | -5.06191 | -0.75357 | 2.32486 |
| H | -4.35172 | 1.26979 | 1.07766 |
| H | -0.96304 | -1.83582 | 2.90061 |
| H | -3.33666 | -2.32116 | 3.19341 |
| H | 3.78578 | 1.67278 | 1.41794 |
| H | 3.29695 | -0.52161 | 2.50541 |
| H | 0.98211 | -1.32552 | 2.61214 |
| C | 2.18873 | 3.27762 | 0.15453 |
| C | 1.43908 | 3.68772 | -1.08979 |
| H | 2.15008 | 4.16048 | -1.76909 |
| H | 0.92459 | 2.84616 | -1.55668 |
| H | 0.66718 | 4.40803 | -0.81364 |
| O | 3.20121 | 3.87550 | 0.48009 |
| N | -0.57107 | 2.46519 | 0.51546 |
| H | -2.02269 | 1.43659 | -0.92627 |
| C | -2.32497 | 0.86023 | -2.06329 |
| O | -1.78487 | 1.44784 | -3.06296 |
| C | -1.79526 | -0.51263 | -1.62661 |
| C | -0.39546 | -0.74522 | -1.47348 |
| C | -2.66505 | -1.53646 | -1.29566 |
| C | 0.07027 | -1.98964 | -0.97449 |
| C | -2.20498 | -2.77816 | -0.83186 |
| H | -3.73267 | -1.38633 | -1.39264 |
| C | 1.49558 | -2.15847 | -0.75696 |
| C | -0.85899 | -3.00293 | -0.66793 |
| C | 1.73508 | 0.11678 | -1.59382 |
| H | -2.91899 | -3.55759 | -0.58931 |
| C | 2.33965 | -1.08314 | -1.08643 |
| C | 2.08410 | -3.31771 | -0.20558 |
| H | -0.52007 | -3.96038 | -0.29319 |
| H | 2.39187 | 0.95459 | -1.83374 |
| C | 3.72852 | -1.16518 | -0.87617 |
| C | 3.44570 | -3.38516 | -0.00091 |
| H | 1.47031 | -4.16561 | 0.07046 |
| C | 4.28142 | -2.30456 | -0.33920 |
| H | 4.34686 | -0.30985 | -1.12964 |
| H | 3.87761 | -4.28255 | 0.42761 |
| H | 5.34925 | -2.37085 | -0.16780 |
| C | -3.85870 | 0.99990 | -1.99361 |
| H | -4.30690 | 0.43947 | -2.82149 |
| H | -4.30419 | 0.66028 | -1.05800 |
| H | -4.08931 | 2.05635 | -2.13979 |
| N | 0.47041 | 0.28953 | -1.76965 |

**Prod:** Hydride transfer results in **16** and **S33**

57

-1416.9002204

| | | | |
|---|---|---|---|
| C | 2.37325 | -2.72111 | -2.41218 |
| C | 2.29733 | -1.34716 | -2.39372 |
| C | 1.09152 | -0.71261 | -2.04508 |
| C | -0.04887 | -1.46795 | -1.71345 |
| C | 0.05442 | -2.87371 | -1.72319 |
| C | 1.24311 | -3.48283 | -2.06848 |
| C | 0.99190 | 0.72101 | -2.02487 |
| C | -1.25756 | -0.74082 | -1.37356 |
| C | -1.21487 | 0.67449 | -1.38825 |
| C | -2.38772 | 1.41105 | -1.07366 |
| C | -3.55770 | 0.73770 | -0.77468 |
| C | -3.59558 | -0.66141 | -0.74720 |
| C | -2.46196 | -1.38659 | -1.03459 |
| H | 1.88019 | 1.29983 | -2.27039 |
| H | 3.30065 | -3.21632 | -2.67342 |
| H | 3.16255 | -0.73636 | -2.62954 |
| H | -0.79698 | -3.48785 | -1.45824 |
| H | 1.30693 | -4.56515 | -2.07127 |
| H | -4.44505 | 1.31688 | -0.54799 |
| H | -4.51311 | -1.17276 | -0.48165 |
| H | -2.50142 | -2.46749 | -0.99321 |
| C | -2.45426 | 2.91828 | -1.02492 |
| C | -1.27372 | 3.72682 | -0.55950 |
| H | -1.64272 | 4.67979 | -0.18036 |
| H | -0.68507 | 3.19667 | 0.19072 |
| H | -0.60764 | 3.90109 | -1.40648 |
| O | -3.50491 | 3.46027 | -1.30669 |
| N | -0.08003 | 1.38108 | -1.73560 |
| H | 2.53972 | 2.80053 | 2.04525 |
| C | 3.10717 | 2.37019 | 1.18901 |
| O | 4.44547 | 2.47544 | 1.31653 |
| C | 2.62440 | 0.89823 | 1.11758 |
| C | 1.29241 | 0.47579 | 1.38605 |
| C | 3.56842 | -0.07040 | 0.83645 |
| C | 0.96007 | -0.90550 | 1.39200 |
| C | 3.23738 | -1.43294 | 0.79640 |
| H | 4.58249 | 0.28454 | 0.68429 |
| C | -0.39279 | -1.29219 | 1.74260 |
| C | 1.95563 | -1.85085 | 1.07560 |
| C | -0.85248 | 1.09269 | 1.98056 |
| H | 3.99870 | -2.16799 | 0.55445 |
| C | -1.30729 | -0.26972 | 2.06165 |
| C | -0.84994 | -2.62775 | 1.78973 |
| H | 1.71944 | -2.90710 | 1.05091 |
| H | -1.57508 | 1.88312 | 2.19250 |
| C | -2.62624 | -0.57768 | 2.44442 |
| C | -2.14560 | -2.91486 | 2.16494 |
| H | -0.18083 | -3.44095 | 1.53845 |
| C | -3.04417 | -1.88767 | 2.50467 |
| H | -3.30575 | 0.23503 | 2.68162 |
| H | -2.47502 | -3.94752 | 2.20169 |
| H | -4.05870 | -2.12935 | 2.79917 |
| C | 2.58200 | 3.10469 | -0.07216 |
| H | 3.13864 | 2.72985 | -0.93881 |
| H | 1.51047 | 2.97278 | -0.24436 |
| H | 2.80808 | 4.16982 | 0.03203 |
| N | 0.34653 | 1.45320 | 1.66887 |




S33

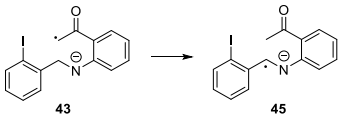
**Prod: S33**

29

-708.7642915

| | | | |
|---|---|---|---|
| H | 2.90016 | -1.53626 | -1.02537 |
| C | 3.23607 | -0.79724 | -0.26243 |
| O | 4.41349 | -0.21043 | -0.55373 |
| C | 2.06507 | 0.20995 | -0.15585 |
| C | 0.69283 | -0.16123 | -0.13494 |
| C | 2.37702 | 1.55290 | -0.07347 |
| C | -0.32240 | 0.82427 | -0.00740 |
| C | 1.38132 | 2.53239 | 0.05705 |
| H | 3.43188 | 1.80073 | -0.12635 |
| C | -1.70733 | 0.39097 | 0.01112 |
| C | 0.04963 | 2.17948 | 0.09379 |
| C | -0.84584 | -1.87945 | -0.24616 |
| H | 1.65888 | 3.57933 | 0.12565 |
| C | -1.96678 | -0.98841 | -0.10789 |
| C | -2.81220 | 1.26157 | 0.14080 |
| H | -0.70519 | 2.94924 | 0.19472 |
| H | -1.05200 | -2.94524 | -0.35080 |
| C | -3.28781 | -1.47663 | -0.09810 |
| C | -4.09989 | 0.77074 | 0.15001 |
| H | -2.65571 | 2.32818 | 0.23466 |
| C | -4.34806 | -0.60926 | 0.03011 |
| H | -3.45220 | -2.54526 | -0.19320 |
| H | -4.93244 | 1.45772 | 0.25069 |
| H | -5.36578 | -0.98066 | 0.03893 |
| C | 3.28402 | -1.57414 | 1.08267 |
| H | 3.53567 | -0.87047 | 1.88336 |
| H | 2.34439 | -2.07965 | 1.32450 |
| H | 4.08645 | -2.31435 | 1.01774 |
| N | 0.38915 | -1.51077 | -0.26008 |

### 7.3 DMSO (Scheme S3.2)



43 45

**SM: 43** abstracting H atom from benzylic position to form **45**

30
-720.1128365

| | | | |
|---|---|---|---|
| C | -2.15076 | 3.48302 | -0.05636 |
| C | -0.98080 | 2.73576 | 0.02377 |
| C | -1.00108 | 1.33810 | 0.03484 |
| C | -2.25489 | 0.72718 | -0.04190 |
| C | -3.43696 | 1.45410 | -0.12376 |
| C | -3.38318 | 2.84458 | -0.12967 |
| H | -2.09768 | 4.56537 | -0.06114 |
| H | -0.01740 | 3.22522 | 0.08266 |
| H | -4.39053 | 0.94485 | -0.18241 |
| H | -4.30176 | 3.41570 | -0.19153 |
| I | -2.42678 | -1.40719 | -0.03936 |
| C | 0.27620 | 0.52989 | 0.12722 |
| H | 0.22201 | -0.15568 | 0.98640 |
| H | 0.34337 | -0.14560 | -0.74046 |
| N | 1.43766 | 1.35966 | 0.23231 |
| C | 2.67008 | 0.83590 | 0.12843 |
| C | 3.71419 | 1.81694 | 0.09168 |
| C | 3.05169 | -0.54910 | -0.00725 |
| C | 5.03058 | 1.48485 | -0.12970 |
| H | 3.41283 | 2.85084 | 0.21586 |
| C | 4.39091 | -0.84291 | -0.25004 |
| C | 5.37603 | 0.14142 | -0.32070 |
| H | 5.79022 | 2.25679 | -0.16538 |
| H | 4.67088 | -1.88520 | -0.35732 |
| H | 6.40717 | -0.13723 | -0.50405 |
| C | 2.11159 | -1.71290 | 0.23056 |
| C | 1.91664 | -2.57833 | -0.81433 |
| H | 1.25185 | -3.42858 | -0.70184 |
| H | 2.41462 | -2.42862 | -1.76366 |
| O | 1.60858 | -1.78321 | 1.40823 |

**TS: 43** abstracting H atom from benzylic position to form **45**

30
-720.0955497

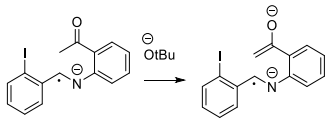
| | | | |
|---|---|---|---|
| C | 2.33489 | 3.38090 | 0.34782 |
| C | 1.11275 | 2.72770 | 0.26375 |
| C | 1.02803 | 1.34363 | 0.05858 |
| C | 2.23805 | 0.65036 | -0.04463 |
| C | 3.47225 | 1.28582 | 0.03397 |
| C | 3.52114 | 2.66208 | 0.23193 |
| H | 2.36188 | 4.45323 | 0.50264 |
| H | 0.18268 | 3.27583 | 0.34837 |
| H | 4.38884 | 0.71602 | -0.05373 |
| H | 4.48083 | 3.16072 | 0.29588 |
| I | 2.26154 | -1.47207 | -0.33030 |
| C | -0.30219 | 0.66172 | 0.00329 |
| H | -0.32318 | -0.15041 | -0.74278 |
| H | -0.41585 | -0.07214 | 0.98565 |
| N | -1.40325 | 1.49114 | -0.00257 |
| C | -2.63689 | 0.90641 | -0.10047 |
| C | -3.68948 | 1.75940 | -0.52765 |
| C | -2.97921 | -0.45438 | 0.18412 |
| C | -4.97858 | 1.30520 | -0.72755 |
| H | -3.43403 | 2.79458 | -0.72630 |
| C | -4.28800 | -0.88675 | -0.03609 |
| C | -5.28970 | -0.03729 | -0.49256 |
| H | -5.74422 | 1.99195 | -1.07099 |
| H | -4.51794 | -1.92559 | 0.17979 |
| H | -6.29502 | -0.40958 | -0.64860 |
| C | -2.04686 | -1.47746 | 0.80687 |
| C | -1.33265 | -1.08840 | 1.95321 |
| H | -0.66803 | -1.80560 | 2.42207 |
| H | -1.67766 | -0.24483 | 2.54078 |
| O | -1.91980 | -2.57952 | 0.22045 |

**Prod: 45** after H atom abstraction from benzylic position

30

-720.1524777

| | | | |
|---|---|---|---|
| C | 2.44456 | 3.28542 | 0.45865 |
| C | 1.19789 | 2.73232 | 0.24976 |
| C | 1.01754 | 1.34617 | -0.05010 |
| C | 2.21776 | 0.58239 | -0.08479 |
| C | 3.46864 | 1.13109 | 0.12671 |
| C | 3.60067 | 2.49745 | 0.39652 |
| H | 2.52610 | 4.34495 | 0.67676 |
| H | 0.30667 | 3.34584 | 0.30108 |
| H | 4.35021 | 0.50224 | 0.08904 |
| H | 4.58173 | 2.92530 | 0.55978 |
| I | 2.14751 | -1.53236 | -0.44900 |
| C | -0.28051 | 0.81407 | -0.26682 |
| H | -0.36059 | -0.25068 | -0.48948 |
| H | -0.12544 | -0.63452 | 2.09108 |
| N | -1.38505 | 1.56286 | -0.23343 |
| C | -2.59991 | 0.95088 | -0.22801 |
| C | -3.69767 | 1.66898 | -0.78175 |
| C | -2.87353 | -0.37384 | 0.24520 |
| C | -4.92955 | 1.08640 | -0.97476 |
| H | -3.51326 | 2.69039 | -1.09653 |
| C | -4.13068 | -0.95491 | -0.00243 |
| C | -5.15536 | -0.25367 | -0.60782 |
| H | -5.72990 | 1.66516 | -1.42358 |
| H | -4.29505 | -1.96824 | 0.34834 |
| H | -6.12280 | -0.71452 | -0.76454 |
| C | -1.97384 | -1.15062 | 1.13288 |
| C | -1.19233 | -0.43302 | 2.21580 |
| H | -1.50881 | -0.85956 | 3.17081 |
| H | -1.35417 | 0.64313 | 2.21496 |
| O | -1.94495 | -2.37363 | 1.09739 |




45 46

**SM: 45** + tert-butoxide anion

44

-953.2772133

| | | | |
|---|---|---|---|
| C | -3.48496 | 3.03921 | -1.47257 |
| C | -2.37228 | 2.62827 | -0.76778 |
| C | -2.26266 | 1.31680 | -0.20688 |
| C | -3.37862 | 0.46897 | -0.45603 |
| C | -4.49483 | 0.87551 | -1.16183 |
| C | -4.56653 | 2.17383 | -1.67933 |
| H | -3.51838 | 4.04751 | -1.87166 |
| H | -1.53896 | 3.30198 | -0.60983 |
| H | -5.31625 | 0.18679 | -1.31863 |
| H | -5.44227 | 2.48896 | -2.23238 |
| I | -3.37969 | -1.55779 | 0.25486 |
| C | -1.10704 | 0.93570 | 0.52443 |
| H | -1.08117 | -0.07484 | 0.93309 |
| H | 0.06821 | -1.23361 | -1.66188 |
| N | -0.09237 | 1.77203 | 0.75566 |
| C | 1.05797 | 1.28493 | 1.30227 |
| C | 1.85883 | 2.18888 | 2.05344 |
| C | 1.51832 | -0.06930 | 1.23282 |
| C | 2.95212 | 1.76956 | 2.78100 |
| H | 1.54781 | 3.22800 | 2.07346 |
| C | 2.60661 | -0.47632 | 2.01944 |
| C | 3.32501 | 0.41524 | 2.79715 |
| H | 3.52005 | 2.49356 | 3.35586 |
| H | 2.91115 | -1.51615 | 1.96059 |
| H | 4.17872 | 0.08236 | 3.37477 |
| C | 1.02958 | -1.07492 | 0.24788 |
| C | 0.85292 | -0.64343 | -1.18511 |
| H | 1.82715 | -0.84708 | -1.66020 |
| H | 0.64060 | 0.41914 | -1.28044 |
| O | 0.93984 | -2.25810 | 0.54652 |
| O | 3.97145 | -0.94344 | -2.07496 |
| C | 5.09637 | -0.37871 | -1.52559 |
| C | 6.19112 | -0.15419 | -2.59419 |
| H | 5.80708 | 0.50917 | -3.37582 |
| H | 7.10387 | 0.29099 | -2.18125 |
| H | 6.45317 | -1.11079 | -3.05799 |
| C | 5.69402 | -1.28349 | -0.42310 |
| H | 5.95374 | -2.25815 | -0.84940 |
| H | 6.59292 | -0.85612 | 0.03682 |
| H | 4.94628 | -1.44115 | 0.36070 |
| C | 4.77849 | 0.99309 | -0.88307 |
| H | 4.37541 | 1.66847 | -1.64550 |
| H | 4.02226 | 0.86842 | -0.09998 |
| H | 5.66212 | 1.46586 | -0.43738 |

**TS: 45** + tert-butoxide anion

44

-953.2692603

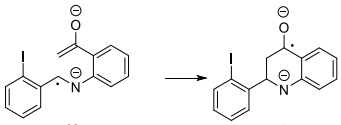
| | | | |
|---|---|---|---|
| C | -2.84406 | 2.63231 | 2.32412 |
| C | -1.84831 | 1.69189 | 2.16351 |
| C | -1.92147 | 0.65453 | 1.17725 |
| C | -3.09393 | 0.69312 | 0.36715 |
| C | -4.09266 | 1.63484 | 0.52171 |
| C | -3.98521 | 2.62236 | 1.51005 |
| H | -2.73598 | 3.39335 | 3.09021 |
| H | -0.96639 | 1.70922 | 2.79185 |
| H | -4.96228 | 1.61430 | -0.12473 |
| H | -4.76964 | 3.35875 | 1.62987 |
| I | -3.37052 | -0.75143 | -1.19714 |
| C | -0.87475 | -0.29501 | 1.05180 |
| H | -0.96361 | -1.04223 | 0.26338 |
| H | 0.56342 | 0.87815 | -1.95839 |
| N | 0.18012 | -0.31031 | 1.86688 |
| C | 1.24140 | -1.12641 | 1.56615 |
| C | 2.01465 | -1.60675 | 2.65456 |
| C | 1.63837 | -1.54621 | 0.26062 |
| C | 3.05630 | -2.49924 | 2.48461 |
| H | 1.73834 | -1.26729 | 3.64726 |
| C | 2.67424 | -2.47555 | 0.11949 |
| C | 3.38754 | -2.96436 | 1.20629 |
| H | 3.61012 | -2.84620 | 3.35087 |
| H | 2.94244 | -2.78348 | -0.88652 |
| H | 4.19651 | -3.67064 | 1.06378 |
| C | 1.12977 | -0.94695 | -1.02836 |
| C | 1.20671 | 0.49341 | -1.16450 |
| H | 2.43987 | 0.71300 | -1.52176 |
| H | 1.08170 | 1.03134 | -0.22658 |
| O | 0.84632 | -1.70574 | -1.96705 |
| O | 3.71339 | 0.97042 | -1.91751 |
| C | 4.39157 | 1.71795 | -0.95551 |
| C | 5.83995 | 1.94755 | -1.41123 |
| H | 5.84924 | 2.48263 | -2.36551 |
| H | 6.41040 | 2.53136 | -0.68080 |
| H | 6.34084 | 0.98530 | -1.55327 |
| C | 4.41063 | 0.97830 | 0.39602 |
| H | 4.90044 | 0.00649 | 0.27665 |
| H | 4.94456 | 1.54615 | 1.16551 |
| H | 3.38871 | 0.79339 | 0.74096 |
| C | 3.71465 | 3.08826 | -0.75916 |
| H | 3.69600 | 3.62958 | -1.70986 |
| H | 2.68285 | 2.95062 | -0.42399 |
| H | 4.23934 | 3.70254 | -0.01991 |

**Prod: 46** + tert-butanol

44

-953.2870449

| | | | |
|---|---|---|---|
| C | -3.03547 | 3.44386 | 0.67746 |
| C | -1.97240 | 2.60221 | 0.92547 |
| C | -2.00857 | 1.19986 | 0.61657 |
| C | -3.22283 | 0.76809 | 0.00369 |
| C | -4.28942 | 1.60702 | -0.24785 |
| C | -4.21747 | 2.96603 | 0.09194 |
| H | -2.95214 | 4.49388 | 0.93971 |
| H | -1.06377 | 2.98025 | 1.37824 |
| H | -5.18630 | 1.21602 | -0.71313 |
| H | -5.05605 | 3.62154 | -0.10508 |
| I | -3.45596 | -1.28108 | -0.60472 |
| C | -0.90348 | 0.36380 | 0.91804 |
| H | -0.98456 | -0.69128 | 0.66096 |
| H | 0.67944 | -0.42880 | -2.46042 |
| N | 0.19246 | 0.81978 | 1.51501 |
| C | 1.26241 | -0.03750 | 1.68696 |
| C | 2.04463 | 0.17271 | 2.84931 |
| C | 1.65730 | -1.09512 | 0.81568 |
| C | 3.10717 | -0.64468 | 3.19161 |
| H | 1.75960 | 0.99843 | 3.49344 |
| C | 2.71597 | -1.92290 | 1.20346 |
| C | 3.44482 | -1.72438 | 2.37117 |
| H | 3.66611 | -0.44896 | 4.10096 |
| H | 2.98428 | -2.73266 | 0.53198 |
| H | 4.26864 | -2.38105 | 2.62631 |
| C | 1.11363 | -1.35428 | -0.58293 |
| C | 1.05884 | -0.28649 | -1.45282 |
| H | 3.16453 | -0.37334 | -1.66286 |
| H | 1.17593 | 0.72544 | -1.08503 |
| O | 0.85297 | -2.57411 | -0.87582 |
| O | 4.13423 | -0.37030 | -1.80909 |
| C | 4.64775 | 0.90588 | -1.42020 |
| C | 6.16489 | 0.78690 | -1.49347 |
| H | 6.47325 | 0.50327 | -2.50283 |
| H | 6.63771 | 1.73861 | -1.24001 |
| H | 6.51810 | 0.02483 | -0.79441 |
| C | 4.20341 | 1.23978 | 0.00436 |
| H | 4.47027 | 0.42978 | 0.68835 |
| H | 4.67506 | 2.16600 | 0.34464 |
| H | 3.11872 | 1.36447 | 0.05019 |
| C | 4.14761 | 1.97460 | -2.39429 |
| H | 4.47065 | 1.73963 | -3.41157 |
| H | 3.05498 | 2.01456 | -2.37643 |
| H | 4.53383 | 2.96101 | -2.12395 |



46 47

**SM: 46** cyclisation from the benzylic
29
-719.6364475

| | | | |
|---|---|---|---|
| C | 2.41851 | 3.31312 | 0.49110 |
| C | 1.18132 | 2.73280 | 0.31111 |
| C | 1.01506 | 1.33434 | 0.02563 |
| C | 2.24113 | 0.60558 | -0.03850 |
| C | 3.48233 | 1.18070 | 0.14420 |
| C | 3.59528 | 2.55316 | 0.41063 |
| H | 2.47870 | 4.37624 | 0.70177 |
| H | 0.27944 | 3.32885 | 0.37797 |
| H | 4.37585 | 0.57016 | 0.08425 |
| H | 4.57002 | 3.00221 | 0.55291 |
| I | 2.22457 | -1.50799 | -0.43230 |
| C | -0.27922 | 0.78251 | -0.16129 |
| H | -0.35243 | -0.28822 | -0.34838 |
| N | -1.37866 | 1.53048 | -0.13435 |
| C | -2.61322 | 0.91403 | -0.21199 |
| C | -3.63984 | 1.65192 | -0.85422 |
| C | -2.95884 | -0.37221 | 0.29795 |
| C | -4.91335 | 1.14622 | -1.05089 |
| H | -3.38352 | 2.64169 | -1.21810 |
| C | -4.24517 | -0.86647 | 0.06173 |
| C | -5.22777 | -0.13897 | -0.60228 |
| H | -5.65909 | 1.74816 | -1.55970 |
| H | -4.47718 | -1.85620 | 0.44460 |
| H | -6.21730 | -0.55543 | -0.75168 |
| C | -2.07514 | -1.26093 | 1.16431 |
| C | -1.66291 | -0.75766 | 2.37158 |
| H | -1.04350 | -1.35804 | 3.03128 |
| H | -1.86720 | 0.27127 | 2.64208 |
| O | -1.85805 | -2.44742 | 0.71759 |

**TS: 46** cyclisation from the benzylic
29
-719.6065580

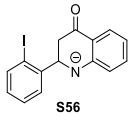
| | | | |
|---|---|---|---|
| C | 2.13213 | 3.33574 | 0.49459 |
| C | 0.94696 | 2.67314 | 0.23573 |
| C | 0.89485 | 1.27778 | -0.05881 |
| C | 2.15685 | 0.62736 | -0.03989 |
| C | 3.34920 | 1.27914 | 0.21509 |
| C | 3.35502 | 2.65351 | 0.48723 |
| H | 2.11100 | 4.40055 | 0.70398 |
| H | 0.00261 | 3.20357 | 0.23761 |
| H | 4.28182 | 0.72742 | 0.20483 |
| H | 4.28815 | 3.16316 | 0.69152 |
| I | 2.28613 | -1.48355 | -0.42771 |
| C | -0.37356 | 0.62165 | -0.23308 |
| H | -0.31917 | -0.37026 | -0.69080 |
| N | -1.48497 | 1.39677 | -0.53297 |
| C | -2.68739 | 0.80472 | -0.36783 |
| C | -3.83903 | 1.39578 | -0.97504 |
| C | -2.92973 | -0.41083 | 0.38415 |
| C | -5.08779 | 0.80585 | -0.94033 |
| H | -3.69254 | 2.32927 | -1.51158 |
| C | -4.19869 | -0.99960 | 0.36198 |
| C | -5.28544 | -0.42452 | -0.28712 |
| H | -5.92116 | 1.29589 | -1.43572 |
| H | -4.32135 | -1.93120 | 0.90827 |
| H | -6.25957 | -0.89905 | -0.27383 |
| C | -1.85278 | -1.02034 | 1.20949 |
| C | -0.84015 | -0.12878 | 1.64275 |
| H | 0.01661 | -0.56174 | 2.15525 |
| H | -1.10344 | 0.88490 | 1.92743 |
| O | -1.78700 | -2.29194 | 1.33863 |

**Prod: 47** cyclised

29

-719.6427170

| | | | |
|---|---|---|---|
| C | 1.99970 | 3.32703 | 0.59693 |
| C | 0.84976 | 2.57504 | 0.39414 |
| C | 0.89358 | 1.20646 | 0.09781 |
| C | 2.16443 | 0.63669 | 0.00725 |
| C | 3.33322 | 1.36881 | 0.19996 |
| C | 3.24991 | 2.72406 | 0.50021 |
| H | 1.92148 | 4.38364 | 0.82647 |
| H | -0.13274 | 3.02809 | 0.44841 |
| H | 4.30044 | 0.88997 | 0.11321 |
| H | 4.15796 | 3.29592 | 0.65049 |
| I | 2.43357 | -1.44364 | -0.46376 |
| C | -0.40898 | 0.43502 | -0.03970 |
| H | -0.22620 | -0.37294 | -0.77201 |
| N | -1.47728 | 1.28848 | -0.50511 |
| C | -2.70574 | 0.74632 | -0.43084 |
| C | -3.79422 | 1.36120 | -1.10177 |
| C | -3.01006 | -0.47613 | 0.32937 |
| C | -5.09384 | 0.81793 | -1.11209 |
| H | -3.58432 | 2.27464 | -1.65286 |
| C | -4.33399 | -1.01725 | 0.26055 |
| C | -5.35778 | -0.38381 | -0.44475 |
| H | -5.88406 | 1.32705 | -1.65639 |
| H | -4.53259 | -1.92839 | 0.81559 |
| H | -6.35424 | -0.81551 | -0.46682 |
| C | -2.03526 | -1.01886 | 1.19862 |
| C | -0.72411 | -0.26584 | 1.29314 |
| H | 0.07473 | -0.96220 | 1.57228 |
| H | -0.77637 | 0.49885 | 2.08570 |
| O | -2.22028 | -2.04319 | 1.95724 |



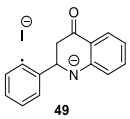

S56

**Product S56**

29

-719.5859468

| | | | |
|---|---|---|---|
| C | 2.01189 | 3.33512 | 0.56672 |
| C | 0.85506 | 2.58962 | 0.37861 |
| C | 0.89470 | 1.22002 | 0.09290 |
| C | 2.15923 | 0.63518 | -0.00006 |
| C | 3.33172 | 1.36397 | 0.17864 |
| C | 3.25638 | 2.72246 | 0.46617 |
| H | 1.94215 | 4.39372 | 0.78799 |
| H | -0.12105 | 3.05479 | 0.43957 |
| H | 4.29617 | 0.87993 | 0.09128 |
| H | 4.16853 | 3.29042 | 0.60492 |
| I | 2.40019 | -1.44823 | -0.44527 |
| C | -0.40626 | 0.45148 | -0.03700 |
| H | -0.25381 | -0.34681 | -0.78492 |
| N | -1.48630 | 1.30283 | -0.49702 |
| C | -2.68299 | 0.75904 | -0.39067 |
| C | -3.81592 | 1.42251 | -1.00356 |
| C | -2.98773 | -0.49000 | 0.28008 |
| C | -5.05855 | 0.85865 | -1.02614 |
| H | -3.63255 | 2.38044 | -1.47941 |
| C | -4.29029 | -1.03935 | 0.22670 |
| C | -5.31971 | -0.40515 | -0.42064 |
| H | -5.86952 | 1.38579 | -1.52009 |
| H | -4.45706 | -1.98122 | 0.74029 |
| H | -6.31323 | -0.83411 | -0.45528 |
| C | -1.99126 | -1.07086 | 1.15069 |
| C | -0.72521 | -0.24675 | 1.29071 |
| H | 0.09066 | -0.88660 | 1.63200 |
| H | -0.90624 | 0.51734 | 2.06010 |
| O | -2.14206 | -2.10661 | 1.80536 |



49

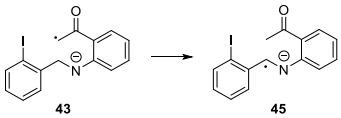
**Product 49**

29

-719.6931479

| | | | |
|---|---|---|---|
| C | 0.53756 | 4.49515 | 0.22893 |
| C | -0.33505 | 3.41199 | 0.10845 |
| C | 0.15365 | 2.10818 | -0.03499 |
| C | 1.52922 | 1.99037 | -0.04976 |
| C | 2.43620 | 3.01471 | 0.05966 |
| C | 1.91685 | 4.30794 | 0.20519 |
| H | 0.13379 | 5.49525 | 0.33863 |
| H | -1.40863 | 3.55810 | 0.11390 |
| H | 3.50616 | 2.83952 | 0.03402 |
| H | 2.58882 | 5.15414 | 0.29464 |
| I | 3.11042 | -1.73631 | -0.29779 |
| C | -0.75268 | 0.89666 | -0.11977 |
| H | -0.32176 | 0.22660 | -0.88977 |
| N | -2.10020 | 1.25415 | -0.51360 |
| C | -2.97896 | 0.28071 | -0.37064 |
| C | -4.31072 | 0.44502 | -0.91796 |
| C | -2.73326 | -0.99135 | 0.28248 |
| C | -5.23050 | -0.56332 | -0.89908 |
| H | -4.54292 | 1.39929 | -1.37957 |
| C | -3.71563 | -2.00854 | 0.27467 |
| C | -4.94294 | -1.82934 | -0.31137 |
| H | -6.20709 | -0.39704 | -1.34443 |
| H | -3.47309 | -2.94131 | 0.77442 |
| H | -5.68763 | -2.61537 | -0.31032 |
| C | -1.54401 | -1.13888 | 1.09244 |
| C | -0.69620 | 0.11307 | 1.19567 |
| H | 0.32799 | -0.16096 | 1.45676 |
| H | -1.10800 | 0.73133 | 2.00660 |
| O | -1.24493 | -2.15477 | 1.72750 |

## 7.4 Benzene (Scheme S3.2)



43 45

**SM: 43** abstracting H atom from benzylic position to form **45**

30
-720.0741434

| | | | |
|---|---|---|---|
| C | -2.14754 | 3.48074 | -0.06301 |
| C | -0.97917 | 2.73399 | 0.03141 |
| C | -0.99835 | 1.33603 | 0.04211 |
| C | -2.25085 | 0.72442 | -0.04808 |
| C | -3.43154 | 1.45203 | -0.14507 |
| C | -3.37923 | 2.84217 | -0.15177 |
| H | -2.09459 | 4.56345 | -0.06660 |
| H | -0.01300 | 3.21684 | 0.10326 |
| H | -4.38288 | 0.93982 | -0.21424 |
| H | -4.29741 | 3.41316 | -0.22533 |
| I | -2.41074 | -1.40783 | -0.03724 |
| C | 0.27860 | 0.53260 | 0.15251 |
| H | 0.22917 | -0.13937 | 1.02595 |
| H | 0.34475 | -0.17006 | -0.69600 |
| N | 1.43500 | 1.36645 | 0.23497 |
| C | 2.66359 | 0.83819 | 0.13695 |
| C | 3.71468 | 1.81308 | 0.09678 |
| C | 3.03761 | -0.54889 | -0.00061 |
| C | 5.02646 | 1.47353 | -0.13159 |
| H | 3.41696 | 2.84739 | 0.22672 |
| C | 4.37481 | -0.84916 | -0.25811 |
| C | 5.36404 | 0.12707 | -0.33086 |
| H | 5.79124 | 2.24119 | -0.16718 |
| H | 4.64253 | -1.89444 | -0.36874 |
| H | 6.39327 | -0.15638 | -0.52000 |
| C | 2.08785 | -1.70411 | 0.23953 |
| C | 1.91254 | -2.57634 | -0.81073 |
| H | 1.22067 | -3.40579 | -0.71399 |
| H | 2.45058 | -2.44700 | -1.74098 |
| O | 1.54777 | -1.75137 | 1.39115 |

**TS: 43** abstracting H atom from benzylic position to form **45**

30
-720.0604115

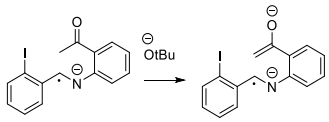
| | | | |
|---|---|---|---|
| C | 2.29903 | 3.40675 | 0.28462 |
| C | 1.08521 | 2.73797 | 0.20822 |
| C | 1.01823 | 1.34913 | 0.03398 |
| C | 2.23608 | 0.66790 | -0.04606 |
| C | 3.46231 | 1.31945 | 0.02436 |
| C | 3.49466 | 2.70013 | 0.19110 |
| H | 2.31261 | 4.48277 | 0.41641 |
| H | 0.14401 | 3.26960 | 0.27598 |
| H | 4.38423 | 0.75559 | -0.04483 |
| H | 4.44820 | 3.21185 | 0.24897 |
| I | 2.26943 | -1.45905 | -0.27190 |
| C | -0.30553 | 0.65076 | -0.01850 |
| H | -0.32346 | -0.12906 | -0.80005 |
| H | -0.39314 | -0.10445 | 0.92572 |
| N | -1.40973 | 1.48302 | 0.00389 |
| C | -2.63963 | 0.90086 | -0.07654 |
| C | -3.71254 | 1.77489 | -0.40663 |
| C | -2.97179 | -0.47578 | 0.14224 |
| C | -5.00863 | 1.33103 | -0.57279 |
| H | -3.46116 | 2.81951 | -0.55360 |
| C | -4.28762 | -0.89658 | -0.04513 |
| C | -5.30956 | -0.02422 | -0.40378 |
| H | -5.78957 | 2.03537 | -0.83876 |
| H | -4.50305 | -1.94905 | 0.11139 |
| H | -6.32081 | -0.38967 | -0.53812 |
| C | -2.01104 | -1.53911 | 0.65217 |
| C | -1.30741 | -1.24981 | 1.83619 |
| H | -0.60515 | -1.98190 | 2.21822 |
| H | -1.67199 | -0.47747 | 2.50373 |
| O | -1.86037 | -2.56432 | -0.04529 |

**Prod: 45** after H atom abstraction from benzylic position

30

-720.1210729

| | | | |
|---|---|---|---|
| C | 2.43364 | 3.28932 | 0.47541 |
| C | 1.19204 | 2.72387 | 0.27932 |
| C | 1.02306 | 1.33695 | -0.02438 |
| C | 2.23112 | 0.58880 | -0.07913 |
| C | 3.47825 | 1.14971 | 0.11943 |
| C | 3.59911 | 2.51540 | 0.39571 |
| H | 2.50509 | 4.34926 | 0.69640 |
| H | 0.29124 | 3.32238 | 0.33937 |
| H | 4.36462 | 0.52875 | 0.06681 |
| H | 4.57728 | 2.95370 | 0.54970 |
| I | 2.17767 | -1.52488 | -0.45209 |
| C | -0.27442 | 0.79790 | -0.23047 |
| H | -0.35383 | -0.26271 | -0.47356 |
| H | -0.15348 | -0.73236 | 2.01148 |
| N | -1.37377 | 1.54629 | -0.17214 |
| C | -2.59369 | 0.95036 | -0.19653 |
| C | -3.67097 | 1.71090 | -0.73596 |
| C | -2.90007 | -0.38529 | 0.22690 |
| C | -4.90666 | 1.15906 | -0.97783 |
| H | -3.45722 | 2.74015 | -1.00266 |
| C | -4.16102 | -0.93247 | -0.07240 |
| C | -5.16019 | -0.19267 | -0.67266 |
| H | -5.68844 | 1.76999 | -1.41739 |
| H | -4.34404 | -1.95714 | 0.23322 |
| H | -6.13024 | -0.63258 | -0.86974 |
| C | -2.04557 | -1.20950 | 1.11738 |
| C | -1.21312 | -0.53329 | 2.19162 |
| H | -1.48777 | -0.99559 | 3.14231 |
| H | -1.36473 | 0.54406 | 2.23304 |
| O | -2.09346 | -2.43098 | 1.09478 |




45 46

**SM: 45** + tert-butoxide anion

44

-953.1685996

| | | | |
|---|---|---|---|
| C | 3.18881 | -0.68751 | 3.36762 |
| C | 2.29844 | 0.12395 | 2.69976 |
| C | 2.19968 | 0.14465 | 1.27027 |
| C | 3.08210 | -0.75482 | 0.60629 |
| C | 3.97454 | -1.57194 | 1.27096 |
| C | 4.04713 | -1.54991 | 2.66962 |
| H | 3.21943 | -0.65968 | 4.45234 |
| H | 1.63354 | 0.78529 | 3.24149 |
| H | 4.61778 | -2.23668 | 0.70671 |
| H | 4.74619 | -2.19354 | 3.18874 |
| I | 3.05321 | -0.90499 | -1.53541 |
| C | 1.27735 | 1.00840 | 0.62623 |
| H | 1.24340 | 0.98973 | -0.46370 |
| H | -0.59509 | -1.17011 | -0.59277 |
| N | 0.50946 | 1.85658 | 1.30568 |
| C | -0.45878 | 2.56426 | 0.65368 |
| C | -0.82741 | 3.81500 | 1.21842 |
| C | -1.11861 | 2.19161 | -0.55858 |
| C | -1.70478 | 4.67586 | 0.59309 |
| H | -0.35549 | 4.08579 | 2.15662 |
| C | -1.97899 | 3.09762 | -1.18899 |
| C | -2.28166 | 4.33383 | -0.63836 |
| H | -1.94233 | 5.62724 | 1.05874 |
| H | -2.44521 | 2.78208 | -2.11673 |
| H | -2.97155 | 5.00518 | -1.13534 |
| C | -1.05966 | 0.82760 | -1.17878 |
| C | -1.28466 | -0.37486 | -0.29991 |
| H | -2.31630 | -0.73151 | -0.46932 |
| H | -1.15572 | -0.14417 | 0.75666 |
| O | -0.96118 | 0.70833 | -2.38844 |
| O | -4.31494 | -1.64377 | -0.63494 |
| C | -5.21375 | -2.14202 | 0.24948 |
| C | -5.83251 | -3.47350 | -0.25715 |
| H | -5.03039 | -4.20177 | -0.41392 |
| H | -6.56793 | -3.90200 | 0.43728 |
| H | -6.32020 | -3.29471 | -1.22100 |
| C | -6.38453 | -1.15159 | 0.49330 |
| H | -6.88320 | -0.94712 | -0.45961 |
| H | -7.12867 | -1.52876 | 1.20782 |
| H | -5.97875 | -0.20842 | 0.87232 |
| C | -4.55808 | -2.43016 | 1.62670 |
| H | -3.74174 | -3.14658 | 1.49043 |
| H | -4.13005 | -1.50268 | 2.01989 |
| H | -5.26292 | -2.83447 | 2.36566 |

**TS: 45** + tert-butoxide anion

44

-953.1630718

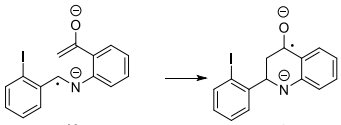
| | | | |
|---|---|---|---|
| C | -2.92502 | 2.68552 | 2.23663 |
| C | -1.89950 | 1.78018 | 2.08322 |
| C | -1.94659 | 0.71371 | 1.12304 |
| C | -3.13418 | 0.69149 | 0.33380 |
| C | -4.16441 | 1.59775 | 0.48141 |
| C | -4.08188 | 2.61542 | 1.44332 |
| H | -2.83022 | 3.46969 | 2.98189 |
| H | -1.00604 | 1.83919 | 2.69254 |
| H | -5.03991 | 1.52580 | -0.15354 |
| H | -4.89053 | 3.32668 | 1.55630 |
| I | -3.37948 | -0.80475 | -1.18629 |
| C | -0.86908 | -0.20260 | 1.01926 |
| H | -0.93892 | -0.98404 | 0.26199 |
| H | 0.64269 | 0.61607 | -2.16150 |
| N | 0.17924 | -0.14493 | 1.83286 |
| C | 1.25358 | -0.97328 | 1.61843 |
| C | 2.00734 | -1.33592 | 2.76423 |
| C | 1.68684 | -1.50509 | 0.36793 |
| C | 3.07121 | -2.21633 | 2.70364 |
| H | 1.69581 | -0.90718 | 3.71093 |
| C | 2.74642 | -2.41425 | 0.33842 |
| C | 3.44534 | -2.78410 | 1.48163 |
| H | 3.61160 | -2.46781 | 3.61124 |
| H | 3.04181 | -2.80253 | -0.63115 |
| H | 4.27822 | -3.47504 | 1.41983 |
| C | 1.18338 | -1.07082 | -0.99507 |
| C | 1.25449 | 0.34364 | -1.29970 |
| H | 2.50891 | 0.54841 | -1.62711 |
| H | 1.07500 | 0.98732 | -0.43899 |
| O | 0.91173 | -1.94682 | -1.82351 |
| O | 3.78798 | 0.79854 | -1.97628 |
| C | 4.40066 | 1.63943 | -1.06263 |
| C | 5.89495 | 1.76293 | -1.40932 |
| H | 6.00303 | 2.14506 | -2.42898 |
| H | 6.42497 | 2.43390 | -0.72206 |
| H | 6.36085 | 0.77399 | -1.36418 |
| C | 4.27565 | 1.09458 | 0.37565 |
| H | 4.69481 | 0.08494 | 0.42359 |
| H | 4.79839 | 1.73064 | 1.10009 |
| H | 3.22426 | 1.02619 | 0.66801 |
| C | 3.76762 | 3.04643 | -1.11245 |
| H | 3.87151 | 3.45546 | -2.12226 |
| H | 2.70088 | 2.97398 | -0.88308 |
| H | 4.23204 | 3.73948 | -0.40073 |

**Prod: 46** + tert-butanol

44

-953.1764289

| | | | |
|---|---|---|---|
| C | -2.47178 | 3.45492 | 0.95624 |
| C | -1.50844 | 2.47631 | 1.04055 |
| C | -1.75349 | 1.11061 | 0.66107 |
| C | -3.07386 | 0.87360 | 0.17291 |
| C | -4.04362 | 1.84977 | 0.08577 |
| C | -3.76332 | 3.16806 | 0.48133 |
| H | -2.22344 | 4.46823 | 1.25826 |
| H | -0.51231 | 2.70314 | 1.40143 |
| H | -5.02760 | 1.59881 | -0.29342 |
| H | -4.52544 | 3.93391 | 0.40900 |
| I | -3.64299 | -1.09682 | -0.47470 |
| C | -0.72682 | 0.14083 | 0.78505 |
| H | -0.92982 | -0.87047 | 0.43220 |
| H | 0.61858 | -0.21617 | -2.73971 |
| N | 0.45020 | 0.43507 | 1.31634 |
| C | 1.44055 | -0.52731 | 1.32441 |
| C | 2.26983 | -0.54038 | 2.47185 |
| C | 1.71378 | -1.48481 | 0.30212 |
| C | 3.24264 | -1.50322 | 2.67882 |
| H | 2.08281 | 0.22593 | 3.21711 |
| C | 2.67309 | -2.47012 | 0.55988 |
| C | 3.43424 | -2.50585 | 1.72443 |
| H | 3.84014 | -1.48081 | 3.58532 |
| H | 2.82627 | -3.20657 | -0.22142 |
| H | 4.17988 | -3.27971 | 1.87206 |
| C | 1.16504 | -1.48568 | -1.12742 |
| C | 0.98953 | -0.25530 | -1.72016 |
| H | 2.98429 | 0.36347 | -1.99273 |
| H | 0.93756 | 0.64667 | -1.12414 |
| O | 1.04607 | -2.61886 | -1.69168 |
| O | 3.83382 | 0.79946 | -2.19275 |
| C | 4.34518 | 1.36367 | -0.99668 |
| C | 5.46870 | 2.29881 | -1.43578 |
| H | 5.06956 | 3.08307 | -2.08397 |
| H | 5.94641 | 2.76495 | -0.56977 |
| H | 6.22317 | 1.73891 | -1.99461 |
| C | 4.89354 | 0.25502 | -0.09418 |
| H | 5.64211 | -0.32875 | -0.63655 |
| H | 5.35602 | 0.67431 | 0.80503 |
| H | 4.08329 | -0.41544 | 0.21530 |
| C | 3.26163 | 2.14824 | -0.25546 |
| H | 2.81859 | 2.89576 | -0.91907 |
| H | 2.46974 | 1.48071 | 0.09853 |
| H | 3.68973 | 2.65853 | 0.61302 |



46 47

**SM: 46** cyclisation from the benzylic
29
-719.5213947

| | | | |
|---|---|---|---|
| C | 2.44423 | 3.31253 | 0.48016 |
| C | 1.20554 | 2.72930 | 0.34339 |
| C | 1.03268 | 1.32898 | 0.05916 |
| C | 2.25982 | 0.60516 | -0.04183 |
| C | 3.50361 | 1.18235 | 0.09757 |
| C | 3.62503 | 2.55810 | 0.35824 |
| H | 2.50635 | 4.37660 | 0.69024 |
| H | 0.29913 | 3.31471 | 0.44013 |
| H | 4.39374 | 0.56967 | 0.01082 |
| H | 4.60296 | 3.01027 | 0.46880 |
| I | 2.22254 | -1.51151 | -0.42084 |
| C | -0.26555 | 0.77938 | -0.09803 |
| H | -0.34557 | -0.28669 | -0.30665 |
| H | -1.00354 | -1.54681 | 2.89207 |
| N | -1.35377 | 1.52962 | -0.02308 |
| C | -2.59751 | 0.93560 | -0.14056 |
| C | -3.59848 | 1.74271 | -0.73619 |
| C | -2.97449 | -0.37854 | 0.27139 |
| C | -4.87804 | 1.28201 | -0.99420 |
| H | -3.30782 | 2.74980 | -1.01795 |
| C | -4.26228 | -0.82563 | -0.03508 |
| C | -5.22013 | -0.02976 | -0.65695 |
| H | -5.60332 | 1.93828 | -1.46621 |
| H | -4.50541 | -1.84293 | 0.25644 |
| H | -6.21259 | -0.41777 | -0.86040 |
| C | -2.13729 | -1.35985 | 1.09542 |
| C | -1.59752 | -0.88702 | 2.26729 |
| H | -1.63236 | 0.16906 | 2.50555 |
| O | -2.09347 | -2.56038 | 0.65429 |

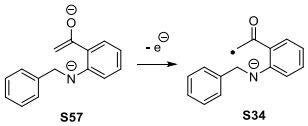
**TS: 46** cyclisation from the benzylic
29
-719.4950127

| | | | |
|---|---|---|---|
| C | 2.04347 | 3.35333 | 0.50594 |
| C | 0.88718 | 2.66654 | 0.20647 |
| C | 0.86924 | 1.26048 | -0.07684 |
| C | 2.15308 | 0.64651 | -0.01345 |
| C | 3.31905 | 1.32281 | 0.27754 |
| C | 3.28965 | 2.70107 | 0.55201 |
| H | 1.98799 | 4.41998 | 0.70520 |
| H | -0.07038 | 3.17186 | 0.16045 |
| H | 4.26123 | 0.78744 | 0.29477 |
| H | 4.20195 | 3.23019 | 0.79829 |
| I | 2.35037 | -1.45933 | -0.43194 |
| C | -0.38012 | 0.58137 | -0.25810 |
| H | -0.30828 | -0.41298 | -0.70875 |
| H | 0.00075 | -0.59963 | 2.14377 |
| N | -1.49765 | 1.34226 | -0.57438 |
| C | -2.69678 | 0.76539 | -0.39695 |
| C | -3.84959 | 1.36095 | -1.00432 |
| C | -2.95209 | -0.43489 | 0.37325 |
| C | -5.10580 | 0.79146 | -0.93680 |
| H | -3.69085 | 2.28113 | -1.55947 |
| C | -4.22600 | -0.99832 | 0.39050 |
| C | -5.31812 | -0.41776 | -0.25202 |
| H | -5.93840 | 1.28582 | -1.43200 |
| H | -4.34587 | -1.91784 | 0.95801 |
| H | -6.30090 | -0.87372 | -0.21056 |
| C | -1.86831 | -1.05935 | 1.19450 |
| C | -0.85500 | -0.16539 | 1.63217 |
| H | -1.12311 | 0.84941 | 1.90620 |
| O | -1.82740 | -2.31477 | 1.33675 |

**Prod: 47** cyclised
Benzene_6mcyc_Prod_SPEofDMSO_att2.log
29
-719.5231012

| | | | |
|---|---|---|---|
| C | 1.99969 | 3.32703 | 0.59693 |
| C | 0.84975 | 2.57504 | 0.39413 |
| C | 0.89357 | 1.20645 | 0.09780 |
| C | 2.16443 | 0.63669 | 0.00724 |
| C | 3.33322 | 1.36880 | 0.19995 |
| C | 3.24990 | 2.72406 | 0.50020 |
| H | 1.92147 | 4.38364 | 0.82646 |
| H | -0.13274 | 3.02808 | 0.44841 |
| H | 4.30043 | 0.88997 | 0.11321 |
| H | 4.15795 | 3.29592 | 0.65049 |
| I | 2.43357 | -1.44364 | -0.46375 |
| C | -0.40897 | 0.43502 | -0.03969 |
| H | -0.22619 | -0.37293 | -0.77200 |
| N | -1.47727 | 1.28847 | -0.50510 |
| C | -2.70573 | 0.74631 | -0.43083 |
| C | -3.79421 | 1.36120 | -1.10177 |
| C | -3.01005 | -0.47612 | 0.32937 |
| C | -5.09384 | 0.81793 | -1.11209 |
| H | -3.58432 | 2.27464 | -1.65286 |
| C | -4.33399 | -1.01725 | 0.26054 |
| C | -5.35778 | -0.38381 | -0.44474 |
| H | -5.88406 | 1.32704 | -1.65638 |
| H | -4.53258 | -1.92839 | 0.81558 |
| H | -6.35424 | -0.81550 | -0.46682 |
| C | -2.03526 | -1.01886 | 1.19862 |
| C | -0.72411 | -0.26583 | 1.29314 |
| H | 0.07473 | -0.96219 | 1.57228 |
| H | -0.77636 | 0.49884 | 2.08570 |
| O | -2.22027 | -2.04318 | 1.95723 |

## 7.5 DMSO (Scheme S3.3)




**SM (Before SET): S57**

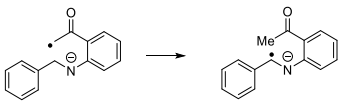
30
-709.4712098

| | | | |
|---|---|---|---|
| C | 4.07685 | -1.49832 | -0.11775 |
| C | 2.70729 | -1.26871 | 0.02669 |
| C | 2.19690 | 0.02885 | 0.04213 |
| C | 3.09822 | 1.09360 | -0.08435 |
| C | 4.46234 | 0.87155 | -0.23158 |
| C | 4.96037 | -0.43219 | -0.24910 |
| H | 4.45349 | -2.51567 | -0.12719 |
| H | 2.00980 | -2.09029 | 0.12954 |
| H | 5.14024 | 1.71235 | -0.33022 |
| H | 6.02366 | -0.61033 | -0.36224 |
| C | 0.71593 | 0.32901 | 0.17890 |
| H | 0.60744 | 1.08895 | 0.96904 |
| H | 0.41052 | 0.85645 | -0.74138 |
| N | -0.07496 | -0.84854 | 0.40560 |
| C | -1.39642 | -0.78917 | 0.21184 |
| C | -2.10642 | -2.04433 | 0.24371 |
| C | -2.23275 | 0.36957 | -0.06366 |
| C | -3.43983 | -2.18029 | -0.08287 |
| H | -1.52200 | -2.92314 | 0.50232 |
| C | -3.57384 | 0.18183 | -0.40837 |
| C | -4.20475 | -1.06290 | -0.44655 |
| H | -3.89356 | -3.16768 | -0.05827 |
| H | -4.15643 | 1.07460 | -0.62108 |
| H | -5.25232 | -1.15298 | -0.70798 |
| C | -1.80197 | 1.80577 | 0.17957 |
| C | -1.89884 | 2.70981 | -0.85573 |
| H | -1.67967 | 3.76057 | -0.68877 |
| H | -2.19646 | 2.39641 | -1.84861 |
| O | -1.43939 | 2.08934 | 1.38204 |
| H | 2.71669 | 2.11128 | -0.06807 |

**Product (After SET): S34**

30
-709.3399758

| | | | |
|---|---|---|---|
| C | -3.85414 | -1.31968 | 0.65750 |
| C | -2.55253 | -1.42403 | 0.17173 |
| C | -1.96847 | -0.36179 | -0.51832 |
| C | -2.70868 | 0.80422 | -0.71378 |
| C | -4.01073 | 0.90966 | -0.23367 |
| C | -4.58827 | -0.15390 | 0.45575 |
| H | -4.29623 | -2.15160 | 1.19426 |
| H | -1.98063 | -2.33011 | 0.33427 |
| H | -4.57040 | 1.82475 | -0.39061 |
| H | -5.60000 | -0.07308 | 0.83575 |
| C | -0.57150 | -0.45759 | -1.09246 |
| C | 1.58147 | -0.82852 | -0.06485 |
| C | 1.99417 | 0.53564 | 0.05563 |
| C | 2.57624 | -1.84165 | 0.04798 |
| C | 3.35950 | 0.81742 | 0.08707 |
| C | 3.91845 | -1.52990 | 0.10854 |
| H | 2.24327 | -2.87283 | 0.01479 |
| C | 4.31933 | -0.18781 | 0.10235 |
| H | 3.65984 | 1.85822 | 0.14686 |
| H | 4.65794 | -2.32092 | 0.15311 |
| H | 5.37217 | 0.06620 | 0.14480 |
| N | 0.32036 | -1.27836 | -0.30067 |
| O | 1.19497 | 2.73081 | -0.42986 |
| C | 1.04286 | 1.68748 | 0.29982 |
| C | 0.16537 | 1.51718 | 1.34006 |
| H | 0.10714 | 0.57882 | 1.87640 |
| H | -0.51589 | 2.31570 | 1.61469 |
| H | -2.25336 | 1.64155 | -1.23372 |
| H | -0.65168 | -0.97944 | -2.06039 |
| H | -0.19287 | 0.54434 | -1.30670 |




S34 S35

**TS S34 to S35**

30

-709.3271991

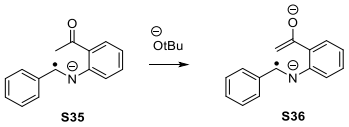
| | | | |
|---|---|---|---|
| C | -4.08760 | -1.26008 | 0.63897 |
| C | -2.70604 | -1.10686 | 0.57605 |
| C | -2.13750 | -0.06522 | -0.16362 |
| C | -2.98894 | 0.82257 | -0.82991 |
| C | -4.37068 | 0.67215 | -0.76586 |
| C | -4.92730 | -0.37192 | -0.03030 |
| H | -4.51248 | -2.07600 | 1.21327 |
| H | -2.05076 | -1.79662 | 1.09445 |
| H | -5.01331 | 1.36760 | -1.29390 |
| H | -6.00310 | -0.49303 | 0.01925 |
| C | -0.65994 | 0.14687 | -0.20844 |
| C | 1.48480 | -0.80446 | -0.00668 |
| C | 2.22963 | 0.41757 | 0.03489 |
| C | 2.23107 | -2.00711 | -0.13334 |
| C | 3.61599 | 0.37676 | -0.12358 |
| C | 3.60509 | -2.01764 | -0.27654 |
| H | 1.66937 | -2.93485 | -0.14514 |
| C | 4.31553 | -0.81364 | -0.28562 |
| H | 4.15405 | 1.31929 | -0.09814 |
| H | 4.12711 | -2.96179 | -0.38601 |
| H | 5.39251 | -0.80627 | -0.40246 |
| N | 0.12621 | -0.95364 | 0.06685 |
| O | 1.89031 | 2.71291 | -0.47437 |
| C | 1.64336 | 1.78443 | 0.33354 |
| C | 0.79893 | 1.89048 | 1.45176 |
| H | 0.84863 | 1.13844 | 2.23142 |
| H | 0.37481 | 2.85799 | 1.69686 |
| H | -2.56055 | 1.63574 | -1.40848 |
| H | -0.35599 | 0.73889 | -1.08969 |
| H | -0.35468 | 0.99940 | 0.62781 |

**Prod S35**

30

-709.3821569

| | | | |
|---|---|---|---|
| C | -4.10915 | -1.18041 | 0.67171 |
| C | -2.73061 | -1.15880 | 0.53141 |
| C | -2.09467 | -0.18625 | -0.28689 |
| C | -2.93248 | 0.75568 | -0.94133 |
| C | -4.30731 | 0.72427 | -0.79016 |
| C | -4.91785 | -0.24490 | 0.01781 |
| H | -4.56651 | -1.93455 | 1.30433 |
| H | -2.11445 | -1.88382 | 1.04935 |
| H | -4.91716 | 1.45969 | -1.30438 |
| H | -5.99434 | -0.26649 | 0.13589 |
| C | -0.67946 | -0.12563 | -0.44157 |
| C | 1.48975 | -0.83536 | 0.05442 |
| C | 2.17167 | 0.42790 | -0.04311 |
| C | 2.31221 | -2.00304 | 0.06623 |
| C | 3.55388 | 0.44439 | -0.32910 |
| C | 3.66450 | -1.94770 | -0.16637 |
| H | 1.81439 | -2.95632 | 0.20969 |
| C | 4.30329 | -0.70971 | -0.40368 |
| H | 4.03105 | 1.41322 | -0.43267 |
| H | 4.24393 | -2.86489 | -0.17764 |
| H | 5.36807 | -0.66675 | -0.59657 |
| N | 0.14879 | -1.02980 | 0.08080 |
| O | 2.00656 | 2.78436 | -0.14552 |
| C | 1.57999 | 1.72951 | 0.31881 |
| C | 0.52799 | 1.79512 | 1.40932 |
| H | 0.34794 | 0.83181 | 1.88370 |
| H | 0.87883 | 2.52026 | 2.14679 |
| H | -2.47580 | 1.51364 | -1.57143 |
| H | -0.28557 | 0.69581 | -1.04961 |
| H | -0.41498 | 2.16161 | 0.99602 |




S35 S36

**S35** + tert-butoxide anion

44

-942.5061170

| | | | |
|---|---|---|---|
| C | -5.15623 | -1.18328 | -1.36036 |
| C | -4.06199 | -0.36016 | -1.14870 |
| C | -3.39764 | -0.33493 | 0.10957 |
| C | -3.90605 | -1.19330 | 1.12373 |
| C | -4.99773 | -2.01059 | 0.89715 |
| C | -5.64250 | -2.01909 | -0.34875 |
| H | -5.64210 | -1.18070 | -2.33113 |
| H | -3.69221 | 0.27803 | -1.94224 |
| H | -5.35730 | -2.65310 | 1.69427 |
| H | -6.49660 | -2.66147 | -0.52492 |
| C | -2.26584 | 0.48802 | 0.36250 |
| C | -0.60649 | 1.99691 | -0.28620 |
| C | 0.45146 | 1.52814 | 0.56455 |
| C | -0.40854 | 3.27159 | -0.89565 |
| C | 1.51193 | 2.39010 | 0.89590 |
| C | 0.66542 | 4.07407 | -0.58644 |
| H | -1.17355 | 3.61515 | -1.58394 |
| C | 1.63426 | 3.65191 | 0.34554 |
| H | 2.27697 | 2.01054 | 1.56559 |
| H | 0.75904 | 5.04666 | -1.05856 |
| H | 2.47527 | 4.28613 | 0.59710 |
| N | -1.78969 | 1.37267 | -0.51865 |
| O | 1.09695 | -0.15269 | 2.09856 |
| C | 0.60623 | 0.12105 | 1.00972 |
| C | 0.32421 | -0.98734 | 0.02231 |
| H | -0.24142 | -0.64684 | -0.84243 |
| H | 1.30051 | -1.36718 | -0.31389 |
| H | -3.41830 | -1.20040 | 2.09447 |
| H | -1.80525 | 0.39293 | 1.35180 |
| H | -0.21160 | -1.79953 | 0.51884 |
| O | 3.32340 | -2.09638 | -1.46702 |
| C | 4.22133 | -1.72206 | -0.49771 |
| C | 5.66618 | -2.12068 | -0.87875 |
| H | 6.39947 | -1.83589 | -0.11498 |
| H | 5.72024 | -3.20463 | -1.02255 |
| H | 5.94488 | -1.63782 | -1.82103 |
| C | 4.19784 | -0.19117 | -0.27924 |
| H | 4.44723 | 0.31666 | -1.21674 |
| H | 3.19134 | 0.11910 | 0.01738 |
| H | 4.90182 | 0.14143 | 0.49312 |
| C | 3.89404 | -2.39040 | 0.85870 |
| H | 2.88912 | -2.09720 | 1.17719 |
| H | 3.91695 | -3.47930 | 0.74450 |
| H | 4.60114 | -2.11144 | 1.64909 |

**S35 TS to S36**

44

-942.4970965

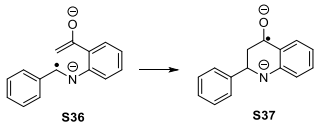
| | | | |
|---|---|---|---|
| C | -5.16113 | -0.93974 | -1.39973 |
| C | -3.99840 | -0.21918 | -1.18319 |
| C | -3.37233 | -0.19867 | 0.09879 |
| C | -3.99728 | -0.96272 | 1.12722 |
| C | -5.15642 | -1.67768 | 0.89434 |
| C | -5.76268 | -1.67851 | -0.37327 |
| H | -5.61208 | -0.93220 | -2.38757 |
| H | -3.54245 | 0.34310 | -1.98929 |
| H | -5.60347 | -2.24540 | 1.70437 |
| H | -6.67207 | -2.23872 | -0.55279 |
| C | -2.18666 | 0.53858 | 0.35698 |
| C | -0.40328 | 1.91135 | -0.27307 |
| C | 0.61060 | 1.37855 | 0.58531 |
| C | -0.12515 | 3.16603 | -0.88143 |
| C | 1.73664 | 2.15250 | 0.88671 |
| C | 1.01428 | 3.89202 | -0.59504 |
| H | -0.87031 | 3.56119 | -1.56429 |
| C | 1.95648 | 3.40178 | 0.32000 |
| H | 2.47554 | 1.72481 | 1.55688 |
| H | 1.17062 | 4.85318 | -1.07420 |
| H | 2.84718 | 3.96956 | 0.56077 |
| N | -1.61927 | 1.34656 | -0.54181 |
| O | 0.99064 | -0.25873 | 2.25753 |
| C | 0.65982 | -0.04592 | 1.08099 |
| C | 0.52760 | -1.09471 | 0.09048 |
| H | -0.14983 | -0.84379 | -0.72454 |
| H | 1.69836 | -1.17350 | -0.49070 |
| H | -3.54637 | -0.97420 | 2.11578 |
| H | -1.76577 | 0.45095 | 1.36398 |
| H | 0.30930 | -2.06878 | 0.53220 |
| O | 2.82548 | -1.26123 | -1.23381 |
| C | 3.92992 | -1.66502 | -0.48601 |
| C | 5.15256 | -1.79065 | -1.40659 |
| H | 6.04636 | -2.10615 | -0.85763 |
| H | 4.95227 | -2.52393 | -2.19346 |
| H | 5.35975 | -0.82696 | -1.88129 |
| C | 4.24232 | -0.63718 | 0.61665 |
| H | 4.42884 | 0.34155 | 0.16363 |
| H | 3.38480 | -0.54279 | 1.28956 |
| H | 5.12075 | -0.92156 | 1.20612 |
| C | 3.66646 | -3.03071 | 0.17650 |
| H | 2.79768 | -2.96058 | 0.83748 |
| H | 3.45253 | -3.78053 | -0.59139 |
| H | 4.52415 | -3.37217 | 0.76547 |

**S36 Product**

44

-942.5143115

| | | | |
|---|---|---|---|
| C | 5.94162 | -0.33798 | 0.33024 |
| C | 4.68996 | 0.25018 | 0.24766 |
| C | 3.53632 | -0.51415 | -0.10542 |
| C | 3.74857 | -1.90260 | -0.35482 |
| C | 5.00217 | -2.47533 | -0.26567 |
| C | 6.12662 | -1.70343 | 0.07775 |
| H | 6.79710 | 0.27498 | 0.59958 |
| H | 4.56722 | 1.30742 | 0.44936 |
| H | 5.11860 | -3.53632 | -0.46405 |
| H | 7.10940 | -2.15342 | 0.14791 |
| C | 2.23145 | 0.04274 | -0.21553 |
| C | 0.73863 | 1.89309 | -0.05478 |
| C | -0.53414 | 1.23982 | 0.05877 |
| C | 0.70683 | 3.31403 | -0.14665 |
| C | -1.69815 | 2.01220 | 0.07495 |
| C | -0.46317 | 4.05106 | -0.14318 |
| H | 1.66559 | 3.81719 | -0.22200 |
| C | -1.69554 | 3.40275 | -0.03026 |
| H | -2.64631 | 1.49205 | 0.18116 |
| H | -0.41638 | 5.13263 | -0.22226 |
| H | -2.62448 | 3.96065 | -0.01658 |
| N | 1.99880 | 1.34568 | -0.03146 |
| O | -0.73895 | -0.92452 | -0.93619 |
| C | -0.73915 | -0.26433 | 0.16023 |
| C | -0.97019 | -0.77628 | 1.41852 |
| H | -0.92014 | -0.14046 | 2.29431 |
| H | -3.07616 | -0.65068 | 1.13743 |
| H | 2.89372 | -2.51759 | -0.62403 |
| H | 1.43815 | -0.64254 | -0.50714 |
| H | -1.09632 | -1.84582 | 1.56072 |
| O | -4.05410 | -0.67620 | 1.15913 |
| C | -4.52189 | -1.33563 | -0.02219 |
| C | -6.01802 | -1.53833 | 0.17797 |
| H | -6.45976 | -2.02214 | -0.69616 |
| H | -6.20253 | -2.16514 | 1.05389 |
| H | -6.51159 | -0.57482 | 0.32829 |
| C | -4.25352 | -0.45380 | -1.24173 |
| H | -4.74461 | 0.51582 | -1.12102 |
| H | -3.17647 | -0.29876 | -1.35516 |
| H | -4.63567 | -0.92592 | -2.15118 |
| C | -3.80362 | -2.67545 | -0.17918 |
| H | -2.73194 | -2.50315 | -0.31723 |
| H | -3.95825 | -3.29242 | 0.71007 |
| H | -4.18498 | -3.21687 | -1.04917 |



S36 S37

**S36** cyclisation to form **S37**

29

-708.8652412

| | | | |
|---|---|---|---|
| C | -4.13028 | -1.34456 | 0.53952 |
| C | -2.75309 | -1.28125 | 0.40870 |
| C | -2.11781 | -0.14793 | -0.18829 |
| C | -2.97957 | 0.90026 | -0.63240 |
| C | -4.35084 | 0.82324 | -0.49114 |
| C | -4.95640 | -0.30236 | 0.09772 |
| H | -4.57775 | -2.22208 | 0.99741 |
| H | -2.13221 | -2.09696 | 0.75946 |
| H | -4.96879 | 1.64535 | -0.83898 |
| H | -6.03240 | -0.36023 | 0.20786 |
| C | -0.70952 | -0.03588 | -0.33703 |
| C | 1.49554 | -0.80771 | -0.02869 |
| C | 2.20222 | 0.43452 | 0.03782 |
| C | 2.28794 | -1.98411 | -0.12522 |
| C | 3.59544 | 0.42907 | -0.05381 |
| C | 3.66925 | -1.95835 | -0.20633 |
| H | 1.75921 | -2.93182 | -0.14844 |
| C | 4.34747 | -0.73718 | -0.18219 |
| H | 4.10699 | 1.38714 | -0.00001 |
| H | 4.21932 | -2.89028 | -0.28931 |
| H | 5.42863 | -0.69547 | -0.24366 |
| N | 0.13426 | -1.00279 | 0.03135 |
| O | 1.38528 | 2.51352 | -0.81705 |
| C | 1.56324 | 1.80212 | 0.23972 |
| C | 1.29043 | 2.17300 | 1.53176 |
| H | 0.84284 | 3.13960 | 1.74422 |
| H | 1.48319 | 1.49794 | 2.35675 |
| H | -2.53377 | 1.78027 | -1.08862 |
| H | -0.34142 | 0.88046 | -0.80056 |

**TS** of **S36** to **S37**

29

-708.8343256

| | | | |
|---|---|---|---|
| C | -3.91162 | -1.23563 | 0.77608 |
| C | -2.54367 | -1.14762 | 0.55276 |
| C | -2.00248 | -0.15769 | -0.30737 |
| C | -2.92261 | 0.73724 | -0.91211 |
| C | -4.28404 | 0.64302 | -0.68258 |
| C | -4.80305 | -0.34786 | 0.16621 |
| H | -4.29355 | -2.00847 | 1.43664 |
| H | -1.86159 | -1.84279 | 1.02809 |
| H | -4.95754 | 1.34247 | -1.16805 |
| H | -5.86902 | -0.42081 | 0.34526 |
| C | -0.58025 | -0.00211 | -0.48905 |
| C | 1.57194 | -0.81587 | -0.11758 |
| C | 2.14843 | 0.49572 | 0.11707 |
| C | 2.50521 | -1.89300 | -0.22274 |
| C | 3.53934 | 0.65424 | 0.08151 |
| C | 3.87424 | -1.70312 | -0.20599 |
| H | 2.09645 | -2.89110 | -0.35747 |
| C | 4.41805 | -0.41116 | -0.07888 |
| H | 3.92543 | 1.66086 | 0.22063 |
| H | 4.53291 | -2.56109 | -0.30544 |
| H | 5.49046 | -0.25428 | -0.08573 |
| N | 0.25197 | -1.08092 | -0.24390 |
| O | 1.61213 | 2.83512 | 0.01451 |
| C | 1.28113 | 1.66216 | 0.42420 |
| C | 0.02131 | 1.35046 | 0.98818 |
| H | -0.67917 | 2.17157 | 1.12954 |
| H | -0.06771 | 0.52745 | 1.69038 |
| H | -2.53980 | 1.51203 | -1.57136 |
| H | -0.30913 | 0.67697 | -1.30961 |

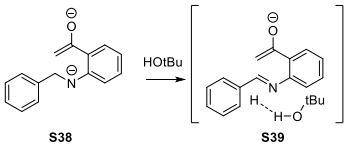
**Product S37**

29

-708.8746445

| | | | |
|---|---|---|---|
| C | 3.88159 | -1.29060 | -0.78141 |
| C | 2.51427 | -1.11552 | -0.56942 |
| C | 2.04077 | -0.07758 | 0.23413 |
| C | 2.97638 | 0.77620 | 0.82860 |
| C | 4.34174 | 0.60590 | 0.62262 |
| C | 4.80174 | -0.43121 | -0.18786 |
| H | 4.22894 | -2.10439 | -1.40906 |
| H | 1.79095 | -1.78814 | -1.01426 |
| H | 5.04839 | 1.27891 | 1.09587 |
| H | 5.86472 | -0.56939 | -0.34952 |
| C | 0.55583 | 0.17263 | 0.42826 |
| C | -1.55658 | -0.81629 | 0.11964 |
| C | -2.17462 | 0.51353 | -0.01231 |
| C | -2.44309 | -1.92360 | 0.16453 |
| C | -3.60369 | 0.61298 | 0.01617 |
| C | -3.84531 | -1.78586 | 0.14808 |
| H | -1.99806 | -2.91262 | 0.24353 |
| C | -4.42443 | -0.51300 | 0.09338 |
| H | -4.04246 | 1.60225 | -0.06514 |
| H | -4.47242 | -2.67133 | 0.19875 |
| H | -5.50486 | -0.40081 | 0.10121 |
| N | -0.22811 | -1.01434 | 0.18688 |
| O | -1.80205 | 2.83178 | -0.48147 |
| C | -1.36053 | 1.63803 | -0.28142 |
| C | 0.12518 | 1.37877 | -0.42319 |
| H | 0.67949 | 2.27713 | -0.12532 |
| H | 0.38118 | 1.17958 | -1.47731 |
| H | 2.62575 | 1.58496 | 1.46407 |
| H | 0.43609 | 0.50368 | 1.48207 |

## 7.6 DMSO (Scheme S3.4)




**S38** + tert-butanol
45
-943.1293587

| | | | |
|---|---|---|---|
| C | -5.23735 | -0.27394 | -0.59614 |
| C | -3.96667 | -0.47743 | -1.13464 |
| C | -2.85164 | 0.17476 | -0.60948 |
| C | -3.03607 | 1.03916 | 0.47325 |
| C | -4.30002 | 1.24833 | 1.01547 |
| C | -5.40740 | 0.59037 | 0.48082 |
| H | -6.09253 | -0.78941 | -1.01892 |
| H | -3.83857 | -1.15349 | -1.97462 |
| H | -4.42485 | 1.92637 | 1.85246 |
| H | -6.39354 | 0.75200 | 0.90100 |
| C | -1.46609 | -0.06119 | -1.16278 |
| H | -1.56862 | -0.48060 | -2.18116 |
| C | 0.55913 | -1.13162 | -0.65825 |
| C | 1.44179 | -1.92094 | 0.18160 |
| C | 1.16364 | -0.61023 | -1.85408 |
| C | 2.75875 | -2.12377 | -0.17749 |
| C | 2.50109 | -0.84983 | -2.18412 |
| H | 0.56126 | -0.03935 | -2.55133 |
| C | 3.32412 | -1.59898 | -1.35760 |
| H | 3.38248 | -2.71272 | 0.49117 |
| H | 2.89449 | -0.43235 | -3.10792 |
| H | 4.36333 | -1.77896 | -1.60608 |
| N | -0.70524 | -0.91594 | -0.28080 |
| O | 0.24402 | -3.64201 | 1.33505 |
| C | 0.93253 | -2.56167 | 1.45785 |
| C | 1.28368 | -1.95994 | 2.64456 |
| H | 1.88426 | -1.05791 | 2.65444 |
| H | 0.95847 | -2.37902 | 3.59316 |
| H | -2.17290 | 1.54908 | 0.89029 |
| O | 2.09105 | 2.38109 | -1.07642 |
| C | 2.10343 | 2.49480 | 0.35317 |
| C | 0.70113 | 2.21858 | 0.89353 |
| H | 0.38264 | 1.20444 | 0.62785 |
| H | 0.68035 | 2.31388 | 1.98299 |
| H | -0.01074 | 2.93251 | 0.46902 |
| C | 2.53080 | 3.92489 | 0.65178 |
| H | 2.57061 | 4.09315 | 1.73025 |
| H | 3.52076 | 4.11875 | 0.23176 |
| H | 1.82084 | 4.63181 | 0.21547 |
| C | 3.10195 | 1.49242 | 0.92888 |
| H | 4.10307 | 1.69105 | 0.53671 |
| H | 3.13435 | 1.56177 | 2.01971 |
| H | 2.81195 | 0.47286 | 0.65411 |
| H | 1.84930 | 1.46629 | -1.29206 |
| H | -0.98122 | 0.92627 | -1.29984 |

**TS** of **S38** to **S39**
45
-943.0712535

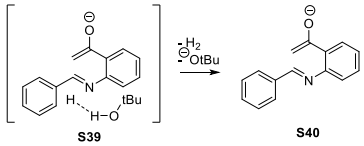
| | | | |
|---|---|---|---|
| C | -2.96816 | -2.69682 | -1.45585 |
| C | -1.78774 | -1.99552 | -1.68319 |
| C | -0.97821 | -1.60934 | -0.61276 |
| C | -1.36355 | -1.93096 | 0.69300 |
| C | -2.53893 | -2.63228 | 0.91887 |
| C | -3.34469 | -3.01525 | -0.15468 |
| H | -3.59260 | -2.99035 | -2.29138 |
| H | -1.49326 | -1.73731 | -2.69552 |
| H | -2.83628 | -2.87698 | 1.93203 |
| H | -4.26556 | -3.55746 | 0.02615 |
| C | 0.25058 | -0.84433 | -0.88645 |
| H | 0.42934 | -0.58526 | -1.93748 |
| H | -1.60185 | 1.64143 | -2.19435 |
| C | 2.14615 | 0.33568 | -0.32007 |
| C | 3.43253 | 0.04241 | 0.16686 |
| C | 1.92286 | 1.49924 | -1.06347 |
| C | 4.46960 | 0.92222 | -0.14080 |
| C | 2.97328 | 2.36577 | -1.35331 |
| H | 0.91156 | 1.73217 | -1.38291 |
| C | 4.25294 | 2.07562 | -0.89448 |
| H | 5.46610 | 0.69192 | 0.22074 |
| H | 2.78506 | 3.26676 | -1.92592 |
| H | 5.07795 | 2.74332 | -1.11458 |
| N | 1.05953 | -0.49581 | 0.02920 |
| O | 3.48487 | -2.32897 | 0.31745 |
| C | 3.70203 | -1.23181 | 0.94435 |
| C | 4.16426 | -1.07967 | 2.22742 |
| H | 4.31413 | -0.09577 | 2.65340 |
| H | 4.38874 | -1.95000 | 2.83592 |
| H | -0.73541 | -1.61692 | 1.51830 |
| H | -2.10082 | 2.09023 | -1.53161 |
| O | -2.80929 | 2.80234 | -0.65617 |
| C | -3.09870 | 2.10073 | 0.51502 |
| C | -3.89236 | 0.81836 | 0.20020 |
| H | -3.29862 | 0.15219 | -0.43247 |
| H | -4.16069 | 0.27088 | 1.11000 |
| H | -4.81234 | 1.07661 | -0.33378 |
| C | -3.94222 | 2.98667 | 1.44291 |
| H | -4.19636 | 2.47193 | 2.37575 |
| H | -3.38984 | 3.89834 | 1.68896 |
| H | -4.87075 | 3.27328 | 0.94034 |
| C | -1.80244 | 1.71116 | 1.24967 |
| H | -1.23382 | 2.61307 | 1.49782 |
| H | -2.00712 | 1.16289 | 2.17604 |
| H | -1.18239 | 1.07749 | 0.61042 |

**Intermediate S39**

45

-943.0842956

| | | | |
|---|---|---|---|
| C | -2.94408 | -2.67901 | -1.46906 |
| C | -1.76638 | -1.97331 | -1.69657 |
| C | -0.95756 | -1.58562 | -0.62589 |
| C | -1.34051 | -1.91086 | 0.67980 |
| C | -2.51243 | -2.61825 | 0.90544 |
| C | -3.31803 | -3.00159 | -0.16798 |
| H | -3.56833 | -2.97307 | -2.30453 |
| H | -1.47384 | -1.71194 | -2.70854 |
| H | -2.80759 | -2.86635 | 1.91840 |
| H | -4.23663 | -3.54770 | 0.01259 |
| C | 0.27176 | -0.82056 | -0.89928 |
| H | 0.45165 | -0.56197 | -1.95060 |
| H | -1.85358 | 1.61560 | -2.64167 |
| C | 2.17225 | 0.35198 | -0.32387 |
| C | 3.45212 | 0.05099 | 0.17583 |
| C | 1.96483 | 1.51615 | -1.07055 |
| C | 4.49807 | 0.92317 | -0.12285 |
| C | 3.02352 | 2.37543 | -1.35128 |
| H | 0.95953 | 1.75867 | -1.40088 |
| C | 4.29657 | 2.07711 | -0.87978 |
| H | 5.48938 | 0.68633 | 0.24852 |
| H | 2.84658 | 3.27700 | -1.92641 |
| H | 5.12799 | 2.73916 | -1.09262 |
| N | 1.07909 | -0.47330 | 0.01842 |
| O | 3.48587 | -2.32020 | 0.32869 |
| C | 3.70520 | -1.22439 | 0.95698 |
| C | 4.15710 | -1.07436 | 2.24392 |
| H | 4.30994 | -0.09123 | 2.67059 |
| H | 4.36978 | -1.94578 | 2.85506 |
| H | -0.71191 | -1.59756 | 1.50510 |
| H | -2.62543 | 2.31243 | -1.34486 |
| O | -3.10956 | 2.81318 | -0.64358 |
| C | -3.15993 | 2.03563 | 0.55201 |
| C | -3.88567 | 0.71488 | 0.28819 |
| H | -3.33081 | 0.10678 | -0.43211 |
| H | -3.98401 | 0.13567 | 1.21045 |
| H | -4.88419 | 0.91069 | -0.11175 |
| C | -3.93413 | 2.87117 | 1.56458 |
| H | -4.00608 | 2.34789 | 2.52105 |
| H | -3.43112 | 3.82750 | 1.72721 |
| H | -4.94460 | 3.06722 | 1.19735 |
| C | -1.74045 | 1.76790 | 1.05643 |
| H | -1.22264 | 2.71278 | 1.24270 |
| H | -1.75789 | 1.18852 | 1.98418 |
| H | -1.17374 | 1.19989 | 0.31446 |




S39 S40

**TS** of **S39** to **S40**

45

-943.0712537

| | | | |
|---|---|---|---|
| C | -2.96849 | -2.69734 | -1.45564 |
| C | -1.78799 | -1.99622 | -1.68312 |
| C | -0.97847 | -1.60983 | -0.61277 |
| C | -1.36388 | -1.93109 | 0.69307 |
| C | -2.53933 | -2.63225 | 0.91907 |
| C | -3.34510 | -3.01540 | -0.15440 |
| H | -3.59293 | -2.99102 | -2.29112 |
| H | -1.49345 | -1.73830 | -2.69551 |
| H | -2.83672 | -2.87668 | 1.93228 |
| H | -4.26602 | -3.55748 | 0.02654 |
| C | 0.25032 | -0.84486 | -0.88659 |
| H | 0.42923 | -0.58628 | -1.93770 |
| H | -1.60184 | 1.64056 | -2.19466 |
| C | 2.14583 | 0.33542 | -0.32023 |
| C | 3.43215 | 0.04226 | 0.16694 |
| C | 1.92268 | 1.49874 | -1.06403 |
| C | 4.46932 | 0.92186 | -0.14096 |
| C | 2.97319 | 2.36511 | -1.35406 |
| H | 0.91143 | 1.73161 | -1.38368 |
| C | 4.25280 | 2.07502 | -0.89505 |
| H | 5.46577 | 0.69161 | 0.22072 |
| H | 2.78507 | 3.26592 | -1.92699 |
| H | 5.07787 | 2.74260 | -1.11531 |
| N | 1.05919 | -0.49596 | 0.02913 |
| O | 3.48456 | -2.32906 | 0.31811 |
| C | 3.70149 | -1.23175 | 0.94483 |
| C | 4.16338 | -1.07930 | 2.22797 |
| H | 4.31307 | -0.09530 | 2.65378 |
| H | 4.38772 | -1.94950 | 2.83673 |
| H | -0.73576 | -1.61689 | 1.51831 |
| H | -2.10032 | 2.08961 | -1.53188 |
| O | -2.80733 | 2.80300 | -0.65600 |
| C | -3.09768 | 2.10155 | 0.51501 |
| C | -3.89171 | 0.81950 | 0.19980 |
| H | -3.29791 | 0.15295 | -0.43241 |
| H | -4.16086 | 0.27225 | 1.10950 |
| H | -4.81123 | 1.07815 | -0.33480 |
| C | -3.94136 | 2.98783 | 1.44243 |
| H | -4.19587 | 2.47336 | 2.37533 |
| H | -3.38894 | 3.89948 | 1.68843 |
| H | -4.86970 | 3.27443 | 0.93950 |
| C | -1.80193 | 1.71156 | 1.25033 |
| H | -1.23321 | 2.61332 | 1.49880 |
| H | -2.00717 | 1.16331 | 2.17659 |
| H | -1.18171 | 1.07779 | 0.61133 |

**Prod S40**

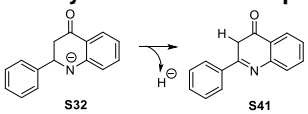
45

-943.0786893

| | | | |
|---|---|---|---|
| C | 3.07899 | -3.99769 | -0.72763 |
| C | 2.23204 | -2.91419 | -0.94389 |
| C | 2.38035 | -1.74282 | -0.19844 |
| C | 3.39198 | -1.66337 | 0.76521 |
| C | 4.23763 | -2.74229 | 0.97739 |
| C | 4.08160 | -3.91276 | 0.23308 |
| H | 2.95635 | -4.90485 | -1.30716 |
| H | 1.44885 | -2.97688 | -1.69299 |
| H | 5.02102 | -2.67529 | 1.72323 |
| H | 4.74312 | -4.75410 | 0.40318 |
| C | 1.46123 | -0.61553 | -0.43995 |
| H | 0.72928 | -0.75630 | -1.24565 |
| H | -0.78823 | -2.44165 | 0.20896 |
| C | 0.54388 | 1.46020 | -0.00928 |
| C | 0.94756 | 2.80630 | -0.06828 |
| C | -0.81251 | 1.12976 | -0.08742 |
| C | -0.03413 | 3.78262 | -0.23488 |
| C | -1.77626 | 2.12112 | -0.24717 |
| H | -1.11183 | 0.09244 | 0.01680 |
| C | -1.38667 | 3.45336 | -0.32552 |
| H | 0.27551 | 4.82078 | -0.29311 |
| H | -2.82328 | 1.84436 | -0.29693 |
| H | -2.12862 | 4.23391 | -0.44917 |
| N | 1.51100 | 0.46024 | 0.23347 |
| O | 3.13925 | 2.73131 | -0.98313 |
| C | 2.41697 | 3.17994 | -0.02335 |
| C | 2.81702 | 3.96732 | 1.02675 |
| H | 2.11126 | 4.29059 | 1.78132 |
| H | 3.85283 | 4.27876 | 1.11568 |
| H | 3.50179 | -0.74927 | 1.33634 |
| H | -1.52296 | -2.34885 | 0.29592 |
| O | -4.27389 | -2.61632 | 0.32458 |
| C | -4.68032 | -1.31566 | 0.17176 |
| C | -4.15006 | -0.42483 | 1.31945 |
| H | -3.05622 | -0.46794 | 1.33857 |
| H | -4.45448 | 0.62413 | 1.22217 |
| H | -4.52143 | -0.80380 | 2.27730 |
| C | -6.22326 | -1.20331 | 0.16751 |
| H | -6.57518 | -0.17075 | 0.05870 |
| H | -6.63154 | -1.79594 | -0.65763 |
| H | -6.61993 | -1.60728 | 1.10464 |
| C | -4.16338 | -0.72052 | -1.15897 |
| H | -4.52160 | -1.33103 | -1.99436 |
| H | -4.49219 | 0.31288 | -1.32166 |
| H | -3.06844 | -0.74151 | -1.16837 |

## 7.7 DMSO (Scheme S3.5)

### 1. Hydride Elimination pathway




**SM S32**

29

-708.8185638

| | | | |
|---|---|---|---|
| C | 4.33215 | 0.59416 | 0.64822 |
| C | 2.96723 | 0.77402 | 0.84986 |
| C | 2.03292 | -0.06256 | 0.23323 |
| C | 2.49720 | -1.08991 | -0.58829 |
| C | 3.86349 | -1.27256 | -0.79468 |
| C | 4.78598 | -0.43179 | -0.17847 |
| H | 5.04198 | 1.25096 | 1.13835 |
| H | 2.61949 | 1.57372 | 1.49776 |
| H | 4.20775 | -2.07661 | -1.43574 |
| H | 5.84850 | -0.57664 | -0.33621 |
| C | 0.55090 | 0.19523 | 0.41572 |
| C | -1.53530 | -0.79846 | 0.13176 |
| C | -2.17683 | 0.49738 | 0.01256 |
| C | -2.43743 | -1.93308 | 0.15084 |
| C | -3.58717 | 0.60838 | 0.02064 |
| C | -3.79342 | -1.77981 | 0.15206 |
| H | -1.99105 | -2.92119 | 0.19861 |
| C | -4.40243 | -0.49152 | 0.10411 |
| H | -4.01112 | 1.60426 | -0.06573 |
| H | -4.42535 | -2.66226 | 0.19037 |
| H | -5.48081 | -0.39403 | 0.10860 |
| N | -0.23858 | -1.00815 | 0.24035 |
| O | -1.79151 | 2.79616 | -0.45597 |
| C | -1.36108 | 1.64988 | -0.29353 |
| C | 0.10892 | 1.34040 | -0.50367 |
| H | 1.77470 | -1.74966 | -1.05350 |
| H | 0.69918 | 2.24416 | -0.33899 |
| H | 0.23987 | 1.03357 | -1.55156 |
| H | 0.40831 | 0.56277 | 1.45105 |

**TS** of **S32** to **S41**

29

-708.7451341

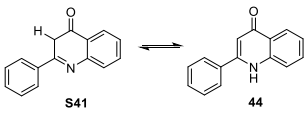
| | | | |
|---|---|---|---|
| C | 3.93692 | -1.44068 | 0.53080 |
| C | 2.56527 | -1.23457 | 0.50288 |
| C | 2.03273 | -0.03996 | 0.00437 |
| C | 2.90731 | 0.93933 | -0.47275 |
| C | 4.28478 | 0.72895 | -0.45271 |
| C | 4.80403 | -0.45761 | 0.05160 |
| H | 4.33514 | -2.36645 | 0.93008 |
| H | 1.88458 | -1.98884 | 0.87826 |
| H | 4.94985 | 1.49530 | -0.83330 |
| H | 5.87545 | -0.61837 | 0.07303 |
| C | 0.55519 | 0.14745 | -0.03861 |
| C | -1.55266 | -0.76893 | -0.17483 |
| C | -2.20432 | 0.45497 | 0.09072 |
| C | -2.34393 | -1.92184 | -0.33320 |
| C | -3.59955 | 0.50766 | 0.19625 |
| C | -3.72173 | -1.85401 | -0.23827 |
| H | -1.84285 | -2.86477 | -0.51962 |
| C | -4.36069 | -0.63492 | 0.03148 |
| H | -4.06540 | 1.46686 | 0.39268 |
| H | -4.31203 | -2.75424 | -0.36663 |
| H | -5.44057 | -0.59049 | 0.10343 |
| N | -0.17480 | -0.91877 | -0.18756 |
| O | -1.87225 | 2.78068 | 0.43657 |
| C | -1.40132 | 1.69128 | 0.15815 |
| C | 0.01939 | 1.53063 | -0.30984 |
| H | 0.63591 | 2.31231 | 0.12463 |
| H | -0.00053 | 1.67379 | -1.40521 |
| H | 2.52452 | 1.86810 | -0.87846 |
| H | 0.12903 | 0.66632 | 2.04534 |

**Product S41**

29

-708.7506846

| | | | |
|---|---|---|---|
| C | 3.95531 | -1.48963 | 0.36020 |
| C | 2.58193 | -1.29730 | 0.31379 |
| C | 2.05053 | -0.05496 | -0.05336 |
| C | 2.92554 | 0.98875 | -0.36989 |
| C | 4.30265 | 0.79137 | -0.33187 |
| C | 4.82081 | -0.44596 | 0.03445 |
| H | 4.35393 | -2.45322 | 0.65481 |
| H | 1.90318 | -2.10111 | 0.56906 |
| H | 4.96816 | 1.60694 | -0.58789 |
| H | 5.89316 | -0.59761 | 0.06968 |
| C | 0.57643 | 0.13321 | -0.09738 |
| C | -1.56587 | -0.76926 | -0.10948 |
| C | -2.23052 | 0.46350 | 0.00646 |
| C | -2.32656 | -1.94004 | -0.18989 |
| C | -3.62463 | 0.51462 | 0.04531 |
| C | -3.71241 | -1.87967 | -0.16193 |
| H | -1.80858 | -2.88816 | -0.27061 |
| C | -4.36855 | -0.65158 | -0.04403 |
| H | -4.10572 | 1.48107 | 0.14164 |
| H | -4.28920 | -2.79481 | -0.22755 |
| H | -5.45051 | -0.61270 | -0.02152 |
| N | -0.16850 | -0.90888 | -0.11302 |
| O | -1.91833 | 2.79115 | 0.30296 |
| C | -1.42915 | 1.69903 | 0.09506 |
| C | 0.05178 | 1.54517 | -0.14428 |
| H | 0.58801 | 2.18818 | 0.55594 |
| H | 0.24339 | 1.95066 | -1.14810 |
| H | 2.54460 | 1.96019 | -0.66053 |
| H | -0.35810 | 0.65009 | 3.17342 |




**SM S41**

28

-708.1012114

| | | | |
|---|---|---|---|
| C | 3.95977 | -1.52775 | -0.15676 |
| C | 2.58660 | -1.33262 | -0.14196 |
| C | 2.05181 | -0.04648 | 0.01069 |
| C | 2.92621 | 1.03626 | 0.14891 |
| C | 4.30377 | 0.83792 | 0.13830 |
| C | 4.82384 | -0.44225 | -0.01577 |
| H | 4.36054 | -2.52703 | -0.27924 |
| H | 1.90869 | -2.16935 | -0.25118 |
| H | 4.96859 | 1.68602 | 0.24905 |
| H | 5.89640 | -0.59583 | -0.02710 |
| C | 0.57603 | 0.14331 | 0.02290 |
| C | -1.56868 | -0.76376 | 0.03068 |
| C | -2.24065 | 0.46937 | -0.01245 |
| C | -2.32177 | -1.94157 | 0.06858 |
| C | -3.63592 | 0.51470 | -0.01929 |
| C | -3.70798 | -1.88757 | 0.06721 |
| H | -1.79724 | -2.88893 | 0.09837 |
| C | -4.37203 | -0.65883 | 0.02378 |
| H | -4.12382 | 1.48171 | -0.05652 |
| H | -4.27940 | -2.80781 | 0.09825 |
| H | -5.45431 | -0.62511 | 0.02275 |
| N | -0.17035 | -0.89738 | 0.02606 |
| O | -1.94966 | 2.81167 | -0.17204 |
| C | -1.44788 | 1.71099 | -0.06388 |
| C | 0.05021 | 1.55618 | 0.04058 |
| H | 0.35413 | 2.03817 | 0.97790 |
| H | 2.54757 | 2.04339 | 0.27094 |
| H | 0.50858 | 2.14570 | -0.75840 |

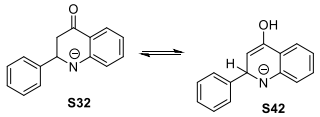
**TS** of **S41** tautomerising to **44**

28

-708.0005752

| | | | |
|---|---|---|---|
| C | 3.86113 | -1.38761 | -0.69882 |
| C | 2.49592 | -1.17757 | -0.53033 |
| C | 2.04481 | -0.02565 | 0.11091 |
| C | 2.96297 | 0.90638 | 0.59485 |
| C | 4.32620 | 0.68968 | 0.43049 |
| C | 4.77756 | -0.45661 | -0.21882 |
| H | 4.20745 | -2.28011 | -1.20619 |
| H | 1.77850 | -1.89998 | -0.89936 |
| H | 5.03512 | 1.41305 | 0.81513 |
| H | 5.84019 | -0.62453 | -0.34765 |
| C | 0.56726 | 0.21581 | 0.25921 |
| C | -1.55725 | -0.75968 | 0.20483 |
| C | -2.17040 | 0.49305 | -0.08162 |
| C | -2.37574 | -1.92045 | 0.33606 |
| C | -3.56660 | 0.55023 | -0.24695 |
| C | -3.72820 | -1.83406 | 0.15607 |
| H | -1.88729 | -2.86009 | 0.56390 |
| C | -4.33112 | -0.58655 | -0.13592 |
| H | -4.01511 | 1.51286 | -0.45899 |
| H | -4.34563 | -2.71994 | 0.24137 |
| H | -5.40540 | -0.53283 | -0.26619 |
| N | -0.22670 | -0.93408 | 0.34912 |
| O | -1.87898 | 2.83299 | -0.39911 |
| C | -1.37443 | 1.72045 | -0.17366 |
| C | 0.02964 | 1.50366 | -0.02390 |
| H | 0.70371 | 2.34734 | -0.11042 |
| H | 2.61746 | 1.79442 | 1.11303 |
| H | 0.31934 | 0.13792 | 1.41003 |

**2. Enol Pathway**




**SM S32**

29

-708.8185638

| | | | |
|---|---|---|---|
| C | 4.33215 | 0.59416 | 0.64822 |
| C | 2.96723 | 0.77402 | 0.84986 |
| C | 2.03292 | -0.06256 | 0.23323 |
| C | 2.49720 | -1.08991 | -0.58829 |
| C | 3.86349 | -1.27256 | -0.79468 |
| C | 4.78598 | -0.43179 | -0.17847 |
| H | 5.04198 | 1.25096 | 1.13835 |
| H | 2.61949 | 1.57372 | 1.49776 |
| H | 4.20775 | -2.07661 | -1.43574 |
| H | 5.84850 | -0.57664 | -0.33621 |
| C | 0.55090 | 0.19523 | 0.41572 |
| C | -1.53530 | -0.79846 | 0.13176 |
| C | -2.17683 | 0.49738 | 0.01256 |
| C | -2.43743 | -1.93308 | 0.15084 |
| C | -3.58717 | 0.60838 | 0.02064 |
| C | -3.79342 | -1.77981 | 0.15206 |
| H | -1.99105 | -2.92119 | 0.19861 |
| C | -4.40243 | -0.49152 | 0.10411 |
| H | -4.01112 | 1.60426 | -0.06573 |
| H | -4.42535 | -2.66226 | 0.19037 |
| H | -5.48081 | -0.39403 | 0.10860 |
| N | -0.23858 | -1.00815 | 0.24035 |
| O | -1.79151 | 2.79616 | -0.45597 |
| C | -1.36108 | 1.64988 | -0.29353 |
| C | 0.10892 | 1.34040 | -0.50367 |
| H | 1.77470 | -1.74966 | -1.05350 |
| H | 0.69918 | 2.24416 | -0.33899 |
| H | 0.23987 | 1.03357 | -1.55156 |
| H | 0.40831 | 0.56277 | 1.45105 |

**TS** of **S32** to **S42**

29

-708.7131734

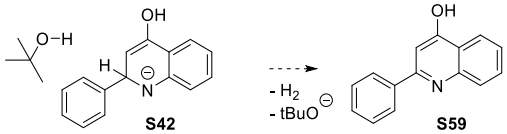
| | | | |
|---|---|---|---|
| C | 4.33989 | 0.56196 | 0.66081 |
| C | 2.97782 | 0.74989 | 0.86950 |
| C | 2.03342 | -0.07040 | 0.24504 |
| C | 2.48666 | -1.08849 | -0.59327 |
| C | 3.85160 | -1.27929 | -0.80770 |
| C | 4.78308 | -0.45601 | -0.18279 |
| H | 5.05693 | 1.20641 | 1.15697 |
| H | 2.63489 | 1.54517 | 1.52494 |
| H | 4.18685 | -2.07662 | -1.46192 |
| H | 5.84385 | -0.60708 | -0.34652 |
| C | 0.55962 | 0.20581 | 0.44412 |
| C | -1.54052 | -0.80475 | 0.11195 |
| C | -2.19775 | 0.50464 | 0.02308 |
| C | -2.44670 | -1.94304 | 0.08236 |
| C | -3.61739 | 0.62313 | 0.09232 |
| C | -3.79561 | -1.78070 | 0.12289 |
| H | -2.00524 | -2.93400 | 0.07083 |
| C | -4.41206 | -0.48241 | 0.15168 |
| H | -4.04845 | 1.61951 | 0.07375 |
| H | -4.43292 | -2.65962 | 0.13649 |
| H | -5.49049 | -0.39805 | 0.19951 |
| N | -0.25445 | -1.00053 | 0.22108 |
| O | -1.60482 | 2.80844 | -0.55478 |
| C | -1.33981 | 1.54916 | -0.30643 |
| C | 0.09850 | 1.37935 | -0.41038 |
| H | 1.75886 | -1.73581 | -1.06759 |
| H | 0.42230 | 0.48822 | 1.50395 |
| H | -0.36335 | 2.81260 | -0.44964 |
| H | 0.37210 | 1.26233 | -1.46911 |

**Product S42**

29

-708.7875514

| | | | |
|---|---|---|---|
| C | -4.39623 | 0.43940 | -0.55700 |
| C | -3.07001 | 0.60165 | -0.94755 |
| C | -2.04281 | -0.10296 | -0.31531 |
| C | -2.37312 | -0.98091 | 0.71561 |
| C | -3.69937 | -1.15052 | 1.10875 |
| C | -4.71604 | -0.43999 | 0.47554 |
| H | -5.18081 | 0.99229 | -1.06166 |
| H | -2.82545 | 1.28222 | -1.75857 |
| H | -3.94025 | -1.84075 | 1.90995 |
| H | -5.74786 | -0.57350 | 0.77942 |
| C | -0.59454 | 0.13700 | -0.72576 |
| C | 1.52989 | -0.81783 | -0.25750 |
| C | 2.13926 | 0.47284 | -0.02183 |
| C | 2.44210 | -1.92936 | -0.22260 |
| C | 3.51679 | 0.60981 | 0.15853 |
| C | 3.79983 | -1.76138 | -0.05580 |
| H | 2.02456 | -2.92246 | -0.35787 |
| C | 4.37075 | -0.48673 | 0.12438 |
| H | 3.91594 | 1.60288 | 0.34011 |
| H | 4.44231 | -2.63747 | -0.06419 |
| H | 5.43950 | -0.36628 | 0.24985 |
| N | 0.23460 | -1.02604 | -0.45390 |
| O | 1.75998 | 2.72211 | 0.67951 |
| C | 1.20874 | 1.57069 | 0.17379 |
| C | -0.10061 | 1.41793 | -0.07335 |
| H | -1.57502 | -1.53561 | 1.19489 |
| H | -0.63335 | 0.30671 | -1.82314 |
| H | 1.07660 | 3.39889 | 0.72775 |
| H | -0.80593 | 2.22068 | 0.12527 |




**S42** **S59**

**SM S42** and tert-butanol

44

-942.4470121

| | | | |
|---|---|---|---|
| C | -1.63293 | 3.82120 | 0.24331 |
| C | -1.02626 | 2.94510 | -0.65326 |
| C | -0.39779 | 1.78091 | -0.20781 |
| C | -0.38360 | 1.51120 | 1.16174 |
| C | -0.98614 | 2.38563 | 2.06345 |
| C | -1.61507 | 3.54285 | 1.60813 |
| H | -2.12576 | 4.71521 | -0.12265 |
| H | -1.05118 | 3.16091 | -1.71813 |
| H | -0.97202 | 2.16061 | 3.12450 |
| H | -2.08798 | 4.21981 | 2.31024 |
| C | 0.27381 | 0.83825 | -1.21509 |
| C | 1.31682 | -1.03705 | -0.15481 |
| C | 2.59982 | -0.38634 | -0.10236 |
| C | 1.24667 | -2.31450 | 0.49027 |
| C | 3.67595 | -0.95637 | 0.58177 |
| C | 2.32437 | -2.84920 | 1.16596 |
| H | 0.30218 | -2.84718 | 0.44678 |
| C | 3.55698 | -2.17621 | 1.23698 |
| H | 4.62291 | -0.42620 | 0.58705 |
| H | 2.21291 | -3.81303 | 1.65445 |
| H | 4.39457 | -2.60412 | 1.77362 |
| N | 0.24542 | -0.54855 | -0.78032 |
| O | 4.01135 | 1.28570 | -1.04960 |
| C | 2.72980 | 0.81380 | -0.91378 |
| C | 1.66554 | 1.36010 | -1.51928 |
| H | 0.08545 | 0.59944 | 1.51491 |
| H | -1.11297 | -1.48592 | -1.03262 |
| H | 1.77148 | 2.22451 | -2.16924 |
| H | -0.32807 | 0.91705 | -2.13105 |
| O | -1.91132 | -2.07816 | -1.22843 |
| C | -2.95546 | -1.74400 | -0.32430 |
| C | -3.44834 | -0.32081 | -0.60421 |
| H | -4.27094 | -0.04996 | 0.06430 |
| H | -2.63285 | 0.39258 | -0.45914 |
| H | -3.80109 | -0.24431 | -1.63667 |
| C | -2.44484 | -1.84427 | 1.11674 |
| H | -2.11006 | -2.86398 | 1.32708 |
| H | -1.59770 | -1.16589 | 1.25201 |
| H | -3.23029 | -1.58093 | 1.83107 |
| C | -4.08174 | -2.74480 | -0.55913 |
| H | -4.92713 | -2.54172 | 0.10349 |
| H | -4.42843 | -2.68418 | -1.59407 |
| H | -3.72697 | -3.76140 | -0.37075 |
| H | 3.99019 | 2.10537 | -1.55437 |

**TS** of **S42** to **S59**

44

-942.3906873

| | | | |
|---|---|---|---|
| C | -4.76810 | 1.30737 | 0.55190 |
| C | -3.41060 | 1.05594 | 0.70017 |
| C | -2.77616 | 0.06541 | -0.05727 |
| C | -3.53969 | -0.66416 | -0.96869 |
| C | -4.90060 | -0.40520 | -1.12923 |
| C | -5.52215 | 0.57746 | -0.36832 |
| H | -5.23925 | 2.08230 | 1.14599 |
| H | -2.82878 | 1.66026 | 1.38721 |
| H | -5.47518 | -0.98109 | -1.84602 |
| H | -6.58040 | 0.77793 | -0.48883 |
| C | -1.31776 | -0.26368 | 0.12839 |
| C | 0.44689 | -1.60678 | -0.51956 |
| C | 1.12973 | -1.43857 | 0.71558 |
| C | 1.11216 | -2.34284 | -1.53554 |
| C | 2.42367 | -1.95726 | 0.89892 |
| C | 2.38181 | -2.83882 | -1.34178 |
| H | 0.59535 | -2.48624 | -2.47805 |
| C | 3.05417 | -2.64386 | -0.11900 |
| H | 2.91724 | -1.80732 | 1.85225 |
| H | 2.87274 | -3.38304 | -2.14140 |
| H | 4.05453 | -3.03557 | 0.02043 |
| N | -0.79342 | -1.11443 | -0.76620 |
| O | 1.01089 | -0.70959 | 2.96970 |
| C | 0.40736 | -0.75704 | 1.75179 |
| C | -0.80053 | -0.21032 | 1.48330 |
| H | -3.05307 | -1.43685 | -1.54966 |
| H | 0.74921 | 1.73625 | 0.15283 |
| H | -1.34608 | 0.32218 | 2.25369 |
| H | -0.78727 | 1.40716 | -0.41334 |
| O | 1.63023 | 1.91502 | 0.55792 |
| C | 2.56817 | 2.21827 | -0.47416 |
| C | 2.20248 | 3.55067 | -1.13097 |
| H | 2.92820 | 3.81795 | -1.90392 |
| H | 1.21432 | 3.48334 | -1.59461 |
| H | 2.18064 | 4.34615 | -0.38181 |
| C | 2.58655 | 1.09888 | -1.51613 |
| H | 2.80141 | 0.14044 | -1.03639 |
| H | 1.61460 | 1.01882 | -2.01113 |
| H | 3.34720 | 1.29535 | -2.27725 |
| C | 3.92414 | 2.31713 | 0.21465 |
| H | 4.70559 | 2.57680 | -0.50344 |
| H | 3.89585 | 3.08402 | 0.99282 |
| H | 4.17741 | 1.35968 | 0.67765 |
| H | 0.47130 | -0.19651 | 3.58109 |

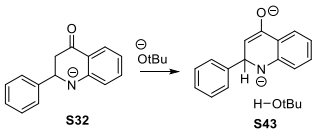
**Product S59** + $H_2$ + tert-butoxide anion

44

-942.4159297

| | | | |
|---|---|---|---|
| C | 4.73228 | 1.24277 | -0.95152 |
| C | 3.56486 | 0.49031 | -1.03603 |
| C | 2.86939 | 0.12988 | 0.12159 |
| C | 3.35933 | 0.54262 | 1.36433 |
| C | 4.53017 | 1.28629 | 1.44825 |
| C | 5.22062 | 1.63825 | 0.29011 |
| H | 5.25701 | 1.52374 | -1.85697 |
| H | 3.18424 | 0.20580 | -2.01040 |
| H | 4.90593 | 1.59138 | 2.41787 |
| H | 6.13255 | 2.22011 | 0.35489 |
| C | 1.61667 | -0.67126 | 0.04763 |
| C | -0.44523 | -1.17796 | 0.92790 |
| C | -0.73226 | -2.10832 | -0.10228 |
| C | -1.42357 | -0.96544 | 1.93371 |
| C | -1.97375 | -2.78619 | -0.12564 |
| C | -2.62182 | -1.63156 | 1.89432 |
| H | -1.19561 | -0.25932 | 2.72380 |
| C | -2.90386 | -2.54827 | 0.85428 |
| H | -2.17414 | -3.48909 | -0.92461 |
| H | -3.36305 | -1.45605 | 2.66544 |
| H | -3.85627 | -3.06394 | 0.83637 |
| N | 0.71732 | -0.46931 | 0.98809 |
| O | 0.00941 | -3.21699 | -2.04710 |
| C | 0.27693 | -2.31434 | -1.08377 |
| C | 1.44821 | -1.60798 | -1.00449 |
| H | 2.81658 | 0.26642 | 2.25996 |
| H | -1.88007 | 1.20288 | -1.67256 |
| H | 2.23512 | -1.76760 | -1.73152 |
| H | -0.45746 | 1.15059 | -2.49842 |
| O | -2.75025 | 1.13906 | -1.20629 |
| C | -2.96652 | 2.31603 | -0.43029 |
| C | -3.18518 | 3.51044 | -1.36136 |
| H | -3.38180 | 4.42194 | -0.79048 |
| H | -2.29769 | 3.67422 | -1.97885 |
| H | -4.03594 | 3.32068 | -2.02049 |
| C | -1.77027 | 2.57237 | 0.48830 |
| H | -1.58401 | 1.69395 | 1.11077 |
| H | -0.87060 | 2.77597 | -0.09831 |
| H | -1.96093 | 3.43115 | 1.13764 |
| C | -4.21703 | 2.04895 | 0.39904 |
| H | -4.46988 | 2.91955 | 1.00904 |
| H | -5.06261 | 1.82523 | -0.25622 |
| H | -4.05208 | 1.19374 | 1.06012 |
| H | 0.74241 | -3.27230 | -2.67103 |

### 3. Enolate formation then hydride elimination




S32 S43

**SM S32** + tert-butoxide anion

43

-941.9423188

| | | | |
|---|---|---|---|
| C | -2.40412 | 2.63236 | 1.03236 |
| C | -1.31683 | 1.78209 | 1.23161 |
| C | -0.36976 | 1.58227 | 0.22737 |
| C | -0.53631 | 2.25193 | -0.98845 |
| C | -1.61898 | 3.09972 | -1.19359 |
| C | -2.55801 | 3.29494 | -0.18044 |
| H | -3.12988 | 2.77524 | 1.82539 |
| H | -1.20161 | 1.26889 | 2.18160 |
| H | -1.73125 | 3.61269 | -2.14239 |
| H | -3.40074 | 3.95808 | -0.33851 |
| C | 0.80288 | 0.64556 | 0.42689 |
| C | 3.10439 | 0.51998 | 0.07980 |
| C | 3.05096 | -0.93002 | 0.06089 |
| C | 4.43697 | 1.08732 | 0.01084 |
| C | 4.23887 | -1.69614 | 0.07878 |
| C | 5.55780 | 0.30803 | 0.02430 |
| H | 4.51486 | 2.16947 | -0.02036 |
| C | 5.48196 | -1.11388 | 0.07697 |
| H | 4.13468 | -2.77696 | 0.06802 |
| H | 6.53329 | 0.78461 | -0.00707 |
| H | 6.38471 | -1.71194 | 0.08779 |
| N | 2.06532 | 1.32626 | 0.17353 |
| O | 1.61549 | -2.79896 | -0.24053 |
| C | 1.77519 | -1.57572 | -0.16546 |
| C | 0.62393 | -0.62414 | -0.41188 |
| H | 0.20158 | 2.11230 | -1.77169 |
| H | -0.33624 | -1.11077 | -0.21407 |
| H | 0.65204 | -0.35545 | -1.47916 |
| H | 0.78605 | 0.32298 | 1.48599 |
| O | -2.49498 | -1.87033 | -0.18338 |
| C | -3.83718 | -1.62297 | -0.03429 |
| C | -4.68765 | -2.83190 | -0.48903 |
| H | -5.76473 | -2.65871 | -0.38015 |
| H | -4.47723 | -3.05186 | -1.54069 |
| H | -4.41760 | -3.71269 | 0.10269 |
| C | -4.27016 | -0.39743 | -0.87279 |
| H | -3.69374 | 0.47968 | -0.55926 |
| H | -4.05657 | -0.58728 | -1.92996 |
| H | -5.33757 | -0.16709 | -0.77172 |
| C | -4.18984 | -1.32971 | 1.44254 |
| H | -5.25830 | -1.13777 | 1.59610 |
| H | -3.89885 | -2.18367 | 2.06318 |
| H | -3.62880 | -0.45299 | 1.78226 |

**TS S32** to **S43**

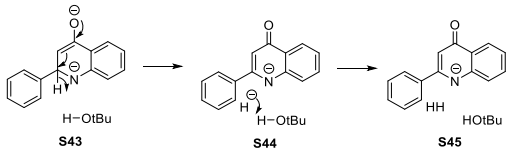
43

-941.9287739

| | | | |
|---|---|---|---|
| C | 4.22704 | -2.19490 | 0.08914 |
| C | 2.84892 | -2.12873 | -0.09427 |
| C | 2.21044 | -0.91742 | -0.37897 |
| C | 2.99735 | 0.23197 | -0.48392 |
| C | 4.37725 | 0.17423 | -0.29276 |
| C | 4.99925 | -1.03837 | -0.00589 |
| H | 4.70035 | -3.14782 | 0.29996 |
| H | 2.25219 | -3.03409 | -0.01784 |
| H | 4.97002 | 1.07930 | -0.37280 |
| H | 6.07293 | -1.08342 | 0.13615 |
| C | 0.68465 | -0.87695 | -0.51095 |
| C | -0.08329 | 1.34072 | -0.78402 |
| C | -0.15658 | 1.56123 | 0.64569 |
| C | -0.40773 | 2.49458 | -1.59481 |
| C | -0.46033 | 2.82702 | 1.16332 |
| C | -0.69801 | 3.71912 | -1.04729 |
| H | -0.39643 | 2.36263 | -2.67270 |
| C | -0.71882 | 3.91974 | 0.35369 |
| H | -0.50082 | 2.92309 | 2.24465 |
| H | -0.91787 | 4.55309 | -1.70861 |
| H | -0.94666 | 4.89212 | 0.77276 |
| N | 0.24755 | 0.20860 | -1.37835 |
| O | -0.09932 | 0.52778 | 2.78694 |
| C | -0.02970 | 0.40182 | 1.54174 |
| C | 0.03786 | -0.88321 | 0.88006 |
| H | 2.51757 | 1.17466 | -0.72160 |
| H | -1.23447 | -1.29345 | 0.80920 |
| H | 0.45747 | -1.65460 | 1.53358 |
| H | 0.41126 | -1.82266 | -1.00177 |
| O | -2.41164 | -1.87291 | 0.89797 |
| C | -3.28299 | -1.54413 | -0.14217 |
| C | -4.63240 | -2.23534 | 0.09515 |
| H | -5.35301 | -2.00444 | -0.69673 |
| H | -4.49407 | -3.31987 | 0.13178 |
| H | -5.05187 | -1.90997 | 1.05167 |
| C | -2.70897 | -2.01146 | -1.49120 |
| H | -1.74937 | -1.51648 | -1.66690 |
| H | -2.54826 | -3.09404 | -1.46872 |
| H | -3.38131 | -1.77907 | -2.32433 |
| C | -3.50321 | -0.02196 | -0.19985 |
| H | -4.18979 | 0.26066 | -1.00516 |
| H | -3.92168 | 0.32592 | 0.75014 |
| H | -2.54587 | 0.48156 | -0.35982 |

**Prod S43** + tert-butanol
43
-941.9454129

| | | | |
|---|---|---|---|
| C | 4.52548 | -1.98616 | 0.02516 |
| C | 3.14025 | -1.99015 | -0.13094 |
| C | 2.42748 | -0.80183 | -0.30538 |
| C | 3.14315 | 0.39854 | -0.33591 |
| C | 4.52635 | 0.41078 | -0.17729 |
| C | 5.22527 | -0.78233 | 0.00574 |
| H | 5.05821 | -2.92203 | 0.15582 |
| H | 2.59921 | -2.93288 | -0.11580 |
| H | 5.06479 | 1.35238 | -0.20102 |
| H | 6.30268 | -0.77316 | 0.12473 |
| C | 0.89457 | -0.81708 | -0.39937 |
| C | -0.09825 | 1.31767 | -0.75664 |
| C | -0.35556 | 1.51750 | 0.65384 |
| C | -0.46519 | 2.42169 | -1.60458 |
| C | -0.87328 | 2.72163 | 1.11838 |
| C | -0.97409 | 3.60579 | -1.10510 |
| H | -0.31725 | 2.30019 | -2.67419 |
| C | -1.17992 | 3.79003 | 0.27158 |
| H | -1.05348 | 2.79719 | 2.18677 |
| H | -1.21770 | 4.40746 | -1.79785 |
| H | -1.57431 | 4.72173 | 0.66003 |
| N | 0.40735 | 0.21583 | -1.30083 |
| O | -0.54867 | 0.48259 | 2.81209 |
| C | -0.18029 | 0.36276 | 1.58092 |
| C | 0.31222 | -0.78731 | 1.00181 |
| H | 2.59891 | 1.32446 | -0.48990 |
| H | -1.68775 | -1.44136 | 0.91602 |
| H | 0.48565 | -1.65866 | 1.63319 |
| H | 0.65818 | -1.79672 | -0.85019 |
| O | -2.55281 | -1.90229 | 0.96478 |
| C | -3.27225 | -1.64127 | -0.24267 |
| C | -4.58143 | -2.41170 | -0.12866 |
| H | -5.19757 | -2.25185 | -1.01667 |
| H | -4.38422 | -3.48205 | -0.02990 |
| H | -5.14199 | -2.07850 | 0.74839 |
| C | -2.45628 | -2.13194 | -1.43861 |
| H | -1.51634 | -1.57458 | -1.49711 |
| H | -2.23660 | -3.19751 | -1.33025 |
| H | -3.00748 | -1.98343 | -2.37133 |
| C | -3.53662 | -0.14023 | -0.36371 |
| H | -4.09822 | 0.08425 | -1.27483 |
| H | -4.11529 | 0.20834 | 0.49636 |
| H | -2.58857 | 0.40520 | -0.39288 |



S43 S44 S45

**SM S43** + tert-butanol
43
-941.9444083

| | | | |
|---|---|---|---|
| C | 4.29886 | -2.23872 | -0.02344 |
| C | 2.92812 | -2.08145 | -0.22709 |
| C | 2.34902 | -0.81331 | -0.29392 |
| C | 3.18199 | 0.30177 | -0.16548 |
| C | 4.55021 | 0.15350 | 0.03819 |
| C | 5.11612 | -1.12015 | 0.11175 |
| H | 4.72882 | -3.23358 | 0.02367 |
| H | 2.29436 | -2.95821 | -0.33460 |
| H | 5.18143 | 1.03057 | 0.13502 |
| H | 6.18260 | -1.23725 | 0.26695 |
| C | 0.83054 | -0.64719 | -0.44611 |
| C | -0.02038 | 1.56129 | -0.77540 |
| C | -0.40837 | 1.71066 | 0.61103 |
| C | -0.27011 | 2.71254 | -1.60380 |
| C | -0.93402 | 2.91038 | 1.07735 |
| C | -0.79039 | 3.89145 | -1.10219 |
| H | -0.01594 | 2.63324 | -2.65712 |
| C | -1.12661 | 4.02337 | 0.25364 |
| H | -1.20507 | 2.95010 | 2.12845 |
| H | -0.93967 | 4.72942 | -1.77856 |
| H | -1.53133 | 4.94966 | 0.64425 |
| N | 0.51131 | 0.47280 | -1.31819 |
| O | -0.71836 | 0.62809 | 2.73311 |
| C | -0.29670 | 0.53005 | 1.51576 |
| C | 0.20232 | -0.61467 | 0.93527 |
| H | 2.73759 | 1.28995 | -0.23250 |
| H | -1.95627 | -1.00363 | 1.03865 |
| H | 0.31990 | -1.50535 | 1.55263 |
| H | 0.50719 | -1.57252 | -0.95750 |
| O | -2.88739 | -1.30076 | 1.05465 |
| C | -3.19198 | -1.83041 | -0.23802 |
| C | -2.33237 | -3.06863 | -0.49469 |
| H | -2.55124 | -3.50015 | -1.47504 |
| H | -1.27301 | -2.79878 | -0.46258 |
| H | -2.52289 | -3.82512 | 0.27091 |
| C | -2.92037 | -0.76437 | -1.29903 |
| H | -3.53259 | 0.12042 | -1.10152 |
| H | -1.86541 | -0.46911 | -1.27857 |
| H | -3.16329 | -1.13923 | -2.29728 |
| C | -4.66876 | -2.20112 | -0.20370 |
| H | -4.98286 | -2.61605 | -1.16425 |
| H | -4.85387 | -2.94576 | 0.57459 |
| H | -5.27431 | -1.31677 | 0.00920 |

**TS1** of **S43** to **S44**

43

-941.9073462

| | | | |
|---|---|---|---|
| C | -4.72378 | 1.36066 | 0.53814 |
| C | -3.37042 | 1.08710 | 0.68388 |
| C | -2.75351 | 0.07267 | -0.05776 |
| C | -3.53542 | -0.65705 | -0.95302 |
| C | -4.89420 | -0.37763 | -1.11236 |
| C | -5.49596 | 0.62871 | -0.36709 |
| H | -5.17926 | 2.15387 | 1.12087 |
| H | -2.76880 | 1.68389 | 1.36108 |
| H | -5.48180 | -0.95477 | -1.81817 |
| H | -6.55095 | 0.84646 | -0.48773 |
| C | -1.29669 | -0.27249 | 0.14052 |
| C | 0.46197 | -1.58546 | -0.56298 |
| C | 1.10739 | -1.50747 | 0.70727 |
| C | 1.16772 | -2.25179 | -1.60688 |
| C | 2.40003 | -2.02371 | 0.87189 |
| C | 2.43947 | -2.74917 | -1.41896 |
| H | 0.67877 | -2.33554 | -2.57265 |
| C | 3.08074 | -2.62956 | -0.17131 |
| H | 2.85363 | -1.93737 | 1.85394 |
| H | 2.95227 | -3.23423 | -2.24391 |
| H | 4.08361 | -3.01634 | -0.03087 |
| N | -0.76255 | -1.07513 | -0.82394 |
| O | 0.85875 | -0.97345 | 3.02718 |
| C | 0.36977 | -0.93048 | 1.84711 |
| C | -0.86610 | -0.38004 | 1.51126 |
| H | -3.06271 | -1.44554 | -1.52455 |
| H | 0.78128 | 1.66852 | 0.24454 |
| H | -1.44831 | 0.09944 | 2.29144 |
| H | -0.79056 | 1.29033 | -0.32671 |
| O | 1.62856 | 1.95390 | 0.65470 |
| C | 2.57366 | 2.26927 | -0.36758 |
| C | 2.16619 | 3.57013 | -1.06243 |
| H | 2.88831 | 3.84345 | -1.83681 |
| H | 1.18492 | 3.45381 | -1.53093 |
| H | 2.10851 | 4.38406 | -0.33526 |
| C | 2.66336 | 1.13023 | -1.38410 |
| H | 2.86685 | 0.18205 | -0.87950 |
| H | 1.72124 | 1.02390 | -1.92837 |
| H | 3.45752 | 1.33003 | -2.10952 |
| C | 3.90968 | 2.44393 | 0.34567 |
| H | 4.69306 | 2.72302 | -0.36303 |
| H | 3.83153 | 3.22602 | 1.10515 |
| H | 4.19691 | 1.51014 | 0.83593 |

**S44 + Hydride anion +** tert-butoxide anion

43

-941.9511334

| | | | |
|---|---|---|---|
| C | -4.29359 | -0.35691 | 0.75613 |
| C | -2.91868 | -0.37921 | 0.97175 |
| C | -2.07856 | -1.15317 | 0.16410 |
| C | -2.65534 | -1.91016 | -0.86135 |
| C | -4.02908 | -1.89483 | -1.07378 |
| C | -4.85523 | -1.11458 | -0.26747 |
| H | -4.92501 | 0.26078 | 1.38472 |
| H | -2.49811 | 0.23503 | 1.75888 |
| H | -4.45719 | -2.49131 | -1.87147 |
| H | -5.92552 | -1.09630 | -0.43680 |
| C | -0.59357 | -1.15539 | 0.34933 |
| C | 1.47608 | -1.44893 | -0.59541 |
| C | 2.14209 | -1.12122 | 0.61272 |
| C | 2.27087 | -1.75721 | -1.73318 |
| C | 3.55054 | -1.10706 | 0.65382 |
| C | 3.64351 | -1.73653 | -1.66884 |
| H | 1.75773 | -2.00465 | -2.65620 |
| C | 4.29888 | -1.40725 | -0.46232 |
| H | 4.02722 | -0.84870 | 1.59267 |
| H | 4.22815 | -1.97446 | -2.55091 |
| H | 5.38172 | -1.39197 | -0.42078 |
| N | 0.12012 | -1.46806 | -0.73212 |
| O | 1.89982 | -0.48168 | 2.89759 |
| C | 1.35463 | -0.78514 | 1.80107 |
| C | -0.04687 | -0.83660 | 1.59629 |
| H | -2.00828 | -2.50544 | -1.49334 |
| H | -0.68879 | -0.61964 | 2.44130 |
| H | -2.33873 | 1.64316 | -2.25097 |
| H | -1.23986 | 2.80547 | -1.71740 |
| O | -0.65182 | 3.56344 | -1.48464 |
| C | 0.17630 | 3.20407 | -0.37781 |
| C | 1.02173 | 4.43327 | -0.06678 |
| H | 1.69325 | 4.23442 | 0.77188 |
| H | 1.62351 | 4.70619 | -0.93727 |
| H | 0.38056 | 5.27928 | 0.19293 |
| C | 1.07028 | 2.02249 | -0.75513 |
| H | 0.46363 | 1.14487 | -0.99531 |
| H | 1.68297 | 2.27698 | -1.62482 |
| H | 1.73102 | 1.75333 | 0.07391 |
| C | -0.69593 | 2.83628 | 0.82352 |
| H | -1.31305 | 1.96609 | 0.58459 |
| H | -0.07831 | 2.58524 | 1.69057 |
| H | -1.35001 | 3.67236 | 1.08510 |

**TS2** of **S44** to **S45**

43

-941.9382458

| | | | |
|---|---|---|---|
| C | -4.51461 | 0.60183 | 0.83251 |
| C | -3.21494 | 0.13101 | 0.99742 |
| C | -2.55143 | -0.51470 | -0.05044 |
| C | -3.21848 | -0.67422 | -1.26896 |
| C | -4.51995 | -0.21313 | -1.43211 |
| C | -5.17344 | 0.42822 | -0.38129 |
| H | -5.01001 | 1.11103 | 1.65137 |
| H | -2.70329 | 0.28916 | 1.94007 |
| H | -5.02584 | -0.35325 | -2.38064 |
| H | -6.18570 | 0.79358 | -0.50924 |
| C | -1.14524 | -0.99470 | 0.10570 |
| C | 0.91857 | -1.28950 | -0.84559 |
| C | 1.47860 | -1.75395 | 0.37216 |
| C | 1.77100 | -1.19137 | -1.97926 |
| C | 2.84627 | -2.09058 | 0.42856 |
| C | 3.10119 | -1.52569 | -1.89902 |
| H | 1.33954 | -0.83251 | -2.90772 |
| C | 3.65346 | -1.97938 | -0.68119 |
| H | 3.24203 | -2.43978 | 1.37589 |
| H | 3.73351 | -1.43834 | -2.77592 |
| H | 4.70467 | -2.23775 | -0.62647 |
| N | -0.38565 | -0.91522 | -0.98511 |
| O | 1.07539 | -2.30618 | 2.65705 |
| C | 0.62745 | -1.87627 | 1.55977 |
| C | -0.71460 | -1.47046 | 1.34859 |
| H | -2.70176 | -1.16458 | -2.08510 |
| H | -1.40851 | -1.53732 | 2.17837 |
| H | -1.20793 | 2.73899 | -1.25177 |
| H | -0.26556 | 2.75093 | -1.15190 |
| O | 1.05604 | 2.75462 | -1.12849 |
| C | 1.64544 | 2.77221 | 0.13789 |
| C | 2.97013 | 1.99487 | 0.10059 |
| H | 3.48607 | 2.02727 | 1.06665 |
| H | 2.77948 | 0.94763 | -0.15593 |
| H | 3.63120 | 2.42383 | -0.65891 |
| C | 0.73209 | 2.11397 | 1.18884 |
| H | -0.21522 | 2.65453 | 1.27130 |
| H | 0.51223 | 1.08168 | 0.89919 |
| H | 1.20833 | 2.10185 | 2.17501 |
| C | 1.93158 | 4.22182 | 0.56846 |
| H | 0.99686 | 4.78955 | 0.60159 |
| H | 2.40449 | 4.27397 | 1.55499 |
| H | 2.59496 | 4.69882 | -0.15946 |

**Product S45 + $H_2$ +** tert-butoxide anion

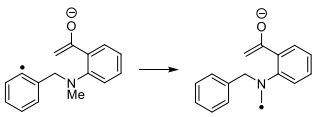
43

-941.9468177

| | | | |
|---|---|---|---|
| C | 4.82143 | -1.97082 | 0.19592 |
| C | 3.55797 | -1.46360 | 0.48603 |
| C | 3.16329 | -0.21133 | 0.00461 |
| C | 4.06314 | 0.51731 | -0.77992 |
| C | 5.32871 | 0.01621 | -1.06283 |
| C | 5.71334 | -1.23139 | -0.57585 |
| H | 5.10724 | -2.94769 | 0.56876 |
| H | 2.86667 | -2.05527 | 1.07530 |
| H | 6.01693 | 0.59982 | -1.66374 |
| H | 6.69830 | -1.62511 | -0.79834 |
| C | 1.80966 | 0.34910 | 0.30253 |
| C | 0.04219 | 1.62887 | -0.39654 |
| C | -0.68231 | 1.38774 | 0.79858 |
| C | -0.56747 | 2.43643 | -1.39486 |
| C | -1.96381 | 1.95011 | 0.96566 |
| C | -1.82016 | 2.97111 | -1.21014 |
| H | -0.01337 | 2.61576 | -2.30996 |
| C | -2.53283 | 2.72988 | -0.01582 |
| H | -2.49044 | 1.74047 | 1.89012 |
| H | -2.26563 | 3.58185 | -1.98787 |
| H | -3.52264 | 3.15087 | 0.11879 |
| N | 1.28584 | 1.12494 | -0.64364 |
| O | -0.68072 | 0.33864 | 2.94057 |
| C | -0.08795 | 0.55681 | 1.84990 |
| C | 1.19383 | 0.04618 | 1.52185 |
| H | 3.75570 | 1.48373 | -1.16000 |
| H | 1.70635 | -0.56214 | 2.25778 |
| H | 0.21948 | -1.62265 | -1.36272 |
| H | -0.51945 | -1.52865 | -1.29777 |
| O | -2.98781 | -1.08576 | -1.57410 |
| C | -3.67476 | -1.68873 | -0.54860 |
| C | -4.76257 | -0.75519 | 0.03361 |
| H | -5.33549 | -1.22658 | 0.84106 |
| H | -4.29339 | 0.15310 | 0.42645 |
| H | -5.45936 | -0.46535 | -0.76000 |
| C | -2.73055 | -2.08109 | 0.61352 |
| H | -1.95765 | -2.76212 | 0.24323 |
| H | -2.23606 | -1.18859 | 1.01304 |
| H | -3.26259 | -2.57686 | 1.43455 |
| C | -4.37634 | -2.98069 | -1.03109 |
| H | -3.62933 | -3.67201 | -1.43473 |
| H | -4.92228 | -3.49183 | -0.22932 |
| H | -5.08452 | -2.73987 | -1.83043 |

## 7. Radical Cyclisation of 18

### 7.1 DMSO (Scheme S4.1)



51 54

**SM 51**

33

-748.6003293

| | | | |
|---|---|---|---|
| C | -4.13227 | 1.19690 | 0.77983 |
| C | -2.81680 | 1.04009 | 0.42253 |
| C | -2.30591 | 0.05521 | -0.39807 |
| C | -3.24156 | -0.85698 | -0.89875 |
| C | -4.59558 | -0.74533 | -0.58005 |
| C | -5.04608 | 0.27272 | 0.25457 |
| H | -4.46101 | 1.99584 | 1.43497 |
| H | -2.90046 | -1.66371 | -1.54054 |
| H | -5.30040 | -1.46484 | -0.98008 |
| H | -6.09802 | 0.35261 | 0.50405 |
| C | -0.83806 | -0.02742 | -0.74943 |
| H | -0.62654 | -0.98364 | -1.24943 |
| H | -0.60023 | 0.77586 | -1.45228 |
| C | 1.32874 | 0.61456 | 0.13190 |
| C | 2.47003 | -0.19974 | 0.00320 |
| C | 1.45782 | 2.00155 | -0.00869 |
| C | 3.70788 | 0.42270 | -0.20283 |
| C | 2.68842 | 2.59745 | -0.25348 |
| H | 0.56369 | 2.60767 | 0.10042 |
| C | 3.82849 | 1.80176 | -0.33338 |
| H | 4.58690 | -0.20638 | -0.29423 |
| H | 2.75861 | 3.67419 | -0.35866 |
| H | 4.80035 | 2.24986 | -0.50701 |
| N | 0.01516 | 0.13415 | 0.42444 |
| O | 1.57793 | -2.18830 | -0.92643 |
| C | 2.39134 | -1.71554 | -0.05384 |
| C | 3.20463 | -2.42287 | 0.79398 |
| H | 3.85361 | -1.91802 | 1.49826 |
| H | 3.20768 | -3.50773 | 0.77014 |
| C | -0.11131 | -0.97044 | 1.36681 |
| H | -1.11379 | -0.94135 | 1.80280 |
| H | 0.04630 | -1.94801 | 0.89635 |
| H | 0.61502 | -0.84267 | 2.16983 |

**TS** of **51** to **54**

33

-748.5874472

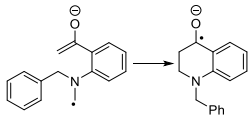
| | | | |
|---|---|---|---|
| C | -3.25610 | -0.84811 | 1.51199 |
| C | -2.21373 | -0.97949 | 0.60979 |
| C | -2.19194 | -0.31976 | -0.60589 |
| C | -3.26499 | 0.51434 | -0.93225 |
| C | -4.32784 | 0.66148 | -0.04262 |
| C | -4.32752 | -0.01503 | 1.17570 |
| H | -3.25278 | -1.37273 | 2.46174 |
| H | -3.26788 | 1.05187 | -1.87643 |
| H | -5.15692 | 1.31086 | -0.29912 |
| H | -5.15583 | 0.10694 | 1.86517 |
| C | -1.01399 | -0.53337 | -1.55586 |
| H | -1.20361 | -1.43267 | -2.15184 |
| H | -0.91559 | 0.29945 | -2.25220 |
| C | 0.95814 | 0.37039 | -0.37787 |
| C | 2.28286 | 0.23029 | 0.10730 |
| C | 0.37999 | 1.64907 | -0.40701 |
| C | 2.95133 | 1.37523 | 0.54211 |
| C | 1.08180 | 2.77363 | 0.01582 |
| H | -0.64078 | 1.77543 | -0.74219 |
| C | 2.37539 | 2.64289 | 0.50125 |
| H | 3.96807 | 1.25903 | 0.90062 |
| H | 0.60308 | 3.74534 | -0.02763 |
| H | 2.93344 | 3.50994 | 0.83460 |
| N | 0.23587 | -0.74936 | -0.84427 |
| O | 3.14215 | -1.67934 | -1.04177 |
| C | 3.05891 | -1.08134 | 0.08715 |
| C | 3.61041 | -1.48385 | 1.27833 |
| H | 3.47980 | -0.90364 | 2.18263 |
| H | 4.19300 | -2.39810 | 1.32713 |
| C | 0.15854 | -1.90893 | -0.02109 |
| H | -0.89872 | -1.72802 | 0.63108 |
| H | -0.02789 | -2.81389 | -0.60325 |
| H | 0.98674 | -2.01423 | 0.67248 |

**Product 54**

33

-748.6348906

| | | | |
|---|---|---|---|
| C | -3.49171 | 0.45919 | 1.48549 |
| C | -2.29102 | 0.09820 | 0.87707 |
| C | -2.28151 | -0.39511 | -0.42580 |
| C | -3.49183 | -0.52527 | -1.11003 |
| C | -4.69100 | -0.16438 | -0.50551 |
| C | -4.69399 | 0.33020 | 0.79711 |
| H | -3.48574 | 0.84038 | 2.50016 |
| H | -3.49314 | -0.91365 | -2.12410 |
| H | -5.62299 | -0.27091 | -1.04855 |
| H | -5.62700 | 0.61010 | 1.27189 |
| C | -0.99511 | -0.78043 | -1.13790 |
| H | -1.12323 | -1.77450 | -1.57849 |
| H | -0.81371 | -0.09186 | -1.96633 |
| C | 1.03773 | 0.30034 | -0.22218 |
| C | 2.41602 | 0.18094 | 0.05991 |
| C | 0.49483 | 1.58048 | -0.43951 |
| C | 3.17656 | 1.34753 | 0.15239 |
| C | 1.28454 | 2.71963 | -0.36934 |
| H | -0.56380 | 1.68749 | -0.64389 |
| C | 2.63714 | 2.61220 | -0.06034 |
| H | 4.23524 | 1.24421 | 0.37035 |
| H | 0.83419 | 3.69055 | -0.54201 |
| H | 3.26245 | 3.49485 | 0.00274 |
| N | 0.19146 | -0.82156 | -0.29952 |
| O | 3.40832 | -1.47166 | 1.46136 |
| C | 3.16629 | -1.13190 | 0.24684 |
| C | 3.54799 | -1.78173 | -0.89536 |
| H | 4.10323 | -2.71272 | -0.83896 |
| H | 3.28553 | -1.39098 | -1.87062 |
| C | 0.31586 | -1.90774 | 0.54028 |
| H | 1.14378 | -1.93634 | 1.22978 |
| H | -0.23041 | -2.79957 | 0.26701 |
| H | -1.35599 | 0.19430 | 1.41801 |




54 S47

**TS** of **54** cyclising to form **S47**

33

-748.6199687

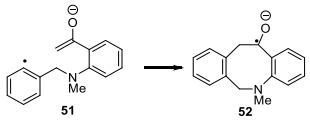
| | | | |
|---|---|---|---|
| C | -3.33798 | 0.39382 | 1.61348 |
| C | -2.18570 | 0.01891 | 0.92489 |
| C | -2.25883 | -0.38226 | -0.40736 |
| C | -3.50257 | -0.40145 | -1.04156 |
| C | -4.65402 | -0.02692 | -0.35694 |
| C | -4.57447 | 0.37203 | 0.97624 |
| H | -3.26786 | 0.70398 | 2.64989 |
| H | -3.56853 | -0.71530 | -2.07926 |
| H | -5.61290 | -0.04815 | -0.86202 |
| H | -5.47017 | 0.66219 | 1.51287 |
| C | -1.01786 | -0.79239 | -1.18521 |
| H | -1.17489 | -1.79515 | -1.59522 |
| H | -0.88716 | -0.12584 | -2.04234 |
| C | 1.03475 | 0.29856 | -0.34941 |
| C | 2.40232 | 0.19374 | 0.04282 |
| C | 0.51017 | 1.58034 | -0.62584 |
| C | 3.13384 | 1.37365 | 0.21714 |
| C | 1.28466 | 2.72160 | -0.49440 |
| H | -0.53123 | 1.68467 | -0.90706 |
| C | 2.60738 | 2.62952 | -0.05067 |
| H | 4.16317 | 1.27109 | 0.54439 |
| H | 0.84527 | 3.68851 | -0.71369 |
| H | 3.21179 | 3.52027 | 0.07332 |
| N | 0.20251 | -0.81573 | -0.40505 |
| O | 3.97694 | -1.19247 | 1.18630 |
| C | 3.10590 | -1.11528 | 0.24676 |
| C | 2.66725 | -2.18565 | -0.52998 |
| H | 3.13298 | -3.15617 | -0.38427 |
| H | 2.15501 | -2.01756 | -1.46801 |
| C | 0.50361 | -1.97702 | 0.31246 |
| H | 0.82893 | -1.84893 | 1.34016 |
| H | -0.14655 | -2.81721 | 0.09996 |
| H | -1.22155 | 0.03628 | 1.42168 |

**Product S47**

33

-748.6938199

| | | | |
|---|---|---|---|
| C | -3.01829 | 0.45070 | 1.68042 |
| C | -1.94970 | 0.10432 | 0.85439 |
| C | -2.17258 | -0.30007 | -0.46083 |
| C | -3.48676 | -0.35082 | -0.93332 |
| C | -4.55461 | -0.00247 | -0.11357 |
| C | -4.32299 | 0.40041 | 1.20018 |
| H | -2.82757 | 0.76242 | 2.70110 |
| H | -3.67289 | -0.66946 | -1.95491 |
| H | -5.56733 | -0.04844 | -0.49751 |
| H | -5.15292 | 0.67049 | 1.84257 |
| C | -1.04195 | -0.69370 | -1.40350 |
| H | -1.29591 | -1.65951 | -1.85091 |
| H | -1.00295 | 0.01928 | -2.23268 |
| C | 1.01813 | 0.33186 | -0.51542 |
| C | 2.30809 | 0.15256 | 0.11682 |
| C | 0.57045 | 1.61073 | -0.81546 |
| C | 3.06263 | 1.33316 | 0.40243 |
| C | 1.35117 | 2.75435 | -0.53402 |
| H | -0.40939 | 1.75099 | -1.25608 |
| C | 2.59514 | 2.59816 | 0.08155 |
| H | 4.03239 | 1.20587 | 0.86954 |
| H | 0.97155 | 3.73784 | -0.78379 |
| H | 3.20072 | 3.46979 | 0.31058 |
| N | 0.27861 | -0.81654 | -0.82995 |
| O | 3.99634 | -1.33312 | 0.89284 |
| C | 2.83888 | -1.13834 | 0.39170 |
| C | 1.99042 | -2.33985 | 0.02773 |
| H | 2.17325 | -3.13280 | 0.75953 |
| H | 2.29659 | -2.72850 | -0.95297 |
| C | 0.51007 | -1.99524 | -0.00033 |
| H | 0.15350 | -1.83468 | 1.02821 |
| H | -0.07252 | -2.81795 | -0.42175 |
| H | -0.93615 | 0.16073 | 1.23351 |




**SM 51** for $S_{RN}1$ cyclisation

33

-748.6017885

| | | | |
|---|---|---|---|
| C | -3.58497 | 1.23402 | 0.50896 |
| C | -2.32613 | 0.81357 | 0.15848 |
| C | -2.01264 | -0.38378 | -0.45232 |
| C | -3.09389 | -1.22640 | -0.73056 |
| C | -4.39768 | -0.85289 | -0.39986 |
| C | -4.64829 | 0.36862 | 0.21766 |
| H | -3.75999 | 2.19156 | 0.98689 |
| H | -2.90822 | -2.18403 | -1.20848 |
| H | -5.21983 | -1.52255 | -0.62291 |
| H | -5.66226 | 0.65413 | 0.47462 |
| C | -0.58992 | -0.74580 | -0.80212 |
| H | -0.58702 | -1.66619 | -1.40845 |
| H | -0.16748 | 0.06057 | -1.39881 |
| C | 1.62403 | -0.64130 | 0.16007 |
| C | 2.02873 | 0.69534 | -0.04826 |
| C | 2.58420 | -1.65779 | 0.13688 |
| C | 3.37077 | 0.95130 | -0.32223 |
| C | 3.92673 | -1.37370 | -0.11083 |
| H | 2.28628 | -2.68568 | 0.30375 |
| C | 4.32396 | -0.06701 | -0.35745 |
| H | 3.67555 | 1.98071 | -0.48278 |
| H | 4.65096 | -2.18041 | -0.12210 |
| H | 5.36329 | 0.16400 | -0.56120 |
| N | 0.24853 | -0.92203 | 0.38862 |
| O | 0.87422 | 2.18813 | 1.38239 |
| C | 1.09035 | 1.87863 | 0.15598 |
| C | 0.62482 | 2.52339 | -0.95945 |
| H | 0.88157 | 2.17483 | -1.95246 |
| H | -0.03153 | 3.38282 | -0.86446 |
| C | -0.05506 | -2.17199 | 1.06539 |
| H | -1.10609 | -2.16120 | 1.36204 |
| H | 0.10489 | -3.05696 | 0.42935 |
| H | 0.55634 | -2.26760 | 1.96350 |

**TS** of **51** to form **52**

33

-748.5990491

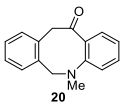
| | | | |
|---|---|---|---|
| C | -3.40678 | 1.36530 | 0.04122 |
| C | -2.17026 | 0.85432 | -0.29235 |
| C | -1.93485 | -0.49576 | -0.50101 |
| C | -3.02070 | -1.36792 | -0.37328 |
| C | -4.28611 | -0.88516 | -0.03424 |
| C | -4.48239 | 0.47681 | 0.17531 |
| H | -3.55806 | 2.42994 | 0.19469 |
| H | -2.87461 | -2.43148 | -0.54419 |
| H | -5.11705 | -1.57422 | 0.06324 |
| H | -5.46658 | 0.85087 | 0.43725 |
| C | -0.54886 | -0.98756 | -0.84279 |
| H | -0.60841 | -1.97245 | -1.33163 |
| H | -0.09797 | -0.29111 | -1.54688 |
| C | 1.65227 | -0.63568 | 0.11220 |
| C | 1.89079 | 0.74724 | -0.01647 |
| C | 2.72347 | -1.52902 | 0.01236 |
| C | 3.18495 | 1.18215 | -0.29586 |
| C | 4.01498 | -1.07103 | -0.24246 |
| H | 2.54973 | -2.59269 | 0.12433 |
| C | 4.24819 | 0.28761 | -0.41499 |
| H | 3.36442 | 2.24880 | -0.39086 |
| H | 4.83044 | -1.78152 | -0.31788 |
| H | 5.24737 | 0.65212 | -0.62366 |
| N | 0.32101 | -1.07787 | 0.34102 |
| O | 0.77148 | 2.11378 | 1.54631 |
| C | 0.82800 | 1.78647 | 0.31183 |
| C | 0.04972 | 2.29664 | -0.70312 |
| H | 0.19271 | 1.98481 | -1.72999 |
| H | -0.63832 | 3.10991 | -0.50229 |
| C | 0.16346 | -2.35025 | 1.02493 |
| H | -0.88180 | -2.45737 | 1.32425 |
| H | 0.42167 | -3.21579 | 0.39512 |
| H | 0.78210 | -2.36996 | 1.92321 |

**Product 52**

33

-748.6670331

| | | | |
|---|---|---|---|
| C | 2.95787 | 1.40855 | -0.15517 |
| C | 1.85409 | 0.75931 | 0.39822 |
| C | 1.88541 | -0.63931 | 0.52352 |
| C | 3.00966 | -1.35001 | 0.11163 |
| C | 4.10612 | -0.69149 | -0.44471 |
| C | 4.07410 | 0.69152 | -0.58514 |
| H | 2.94683 | 2.49079 | -0.24150 |
| H | 3.02545 | -2.43011 | 0.22391 |
| H | 4.97574 | -1.25488 | -0.76305 |
| H | 4.92049 | 1.21516 | -1.01513 |
| C | 0.63948 | -1.34340 | 0.99464 |
| H | 0.87288 | -2.37664 | 1.27923 |
| H | 0.21994 | -0.86235 | 1.87900 |
| C | -1.59823 | -0.66753 | 0.07743 |
| C | -1.66647 | 0.77410 | -0.01274 |
| C | -2.77357 | -1.41284 | 0.10614 |
| C | -2.97452 | 1.32148 | -0.19740 |
| C | -4.04357 | -0.83264 | -0.00230 |
| H | -2.69584 | -2.49347 | 0.16572 |
| C | -4.12393 | 0.55357 | -0.17872 |
| H | -3.04176 | 2.39391 | -0.33613 |
| H | -4.93309 | -1.45093 | 0.01638 |
| H | -5.09030 | 1.03319 | -0.30057 |
| N | -0.35740 | -1.34437 | -0.08113 |
| O | -0.69001 | 2.85996 | -0.55717 |
| C | -0.56404 | 1.70821 | -0.01184 |
| C | 0.66430 | 1.54150 | 0.89808 |
| H | 0.34790 | 1.12905 | 1.86157 |
| H | 0.99291 | 2.56542 | 1.08946 |
| C | -0.36045 | -2.59636 | -0.81633 |
| H | 0.65895 | -2.80423 | -1.15510 |
| H | -0.69286 | -3.45837 | -0.21674 |
| H | -1.00274 | -2.51363 | -1.69370 |



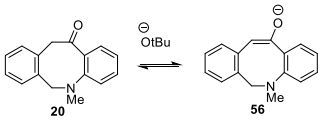

20

**SM 20**

33

-748.5884117

| | | | |
|---|---|---|---|
| C | 3.04806 | -1.38735 | 0.00123 |
| C | 1.86468 | -0.78877 | -0.42655 |
| C | 1.79792 | 0.60921 | -0.52760 |
| C | 2.92181 | 1.37327 | -0.22202 |
| C | 4.10299 | 0.76875 | 0.20234 |
| C | 4.16347 | -0.61483 | 0.31871 |
| H | 3.10054 | -2.46822 | 0.07693 |
| H | 2.86968 | 2.45336 | -0.31644 |
| H | 4.96882 | 1.37552 | 0.44008 |
| H | 5.07709 | -1.09627 | 0.64707 |
| C | 0.49598 | 1.26968 | -0.90450 |
| H | 0.68146 | 2.29386 | -1.24513 |
| H | 0.02377 | 0.74616 | -1.73878 |
| C | -1.67024 | 0.63501 | 0.05914 |
| C | -1.68171 | -0.77066 | 0.01954 |
| C | -2.89174 | 1.31199 | -0.00656 |
| C | -2.88263 | -1.46177 | -0.12241 |
| C | -4.08673 | 0.61359 | -0.15087 |
| H | -2.90771 | 2.39323 | 0.05231 |
| C | -4.08822 | -0.77466 | -0.22437 |
| H | -2.87068 | -2.54618 | -0.13112 |
| H | -5.01973 | 1.16211 | -0.20838 |
| H | -5.01746 | -1.31925 | -0.33656 |
| N | -0.43937 | 1.30592 | 0.23614 |
| O | -0.34289 | -2.23742 | 1.27771 |
| C | -0.43466 | -1.58168 | 0.26482 |
| C | 0.66873 | -1.64565 | -0.78669 |
| H | 0.26623 | -1.36307 | -1.76101 |
| H | 0.98028 | -2.69052 | -0.83399 |
| C | -0.47932 | 2.60771 | 0.88600 |
| H | 0.53490 | 2.87156 | 1.19266 |
| H | -0.85457 | 3.40450 | 0.22835 |
| H | -1.10434 | 2.55818 | 1.77807 |




**Opt SM 20** + tert-butoxide anion
47
-981.7268409

| | | | |
|---|---|---|---|
| C | 0.50269 | 2.97545 | 0.01083 |
| C | -0.31472 | 1.84961 | -0.08191 |
| C | -1.69754 | 2.01813 | -0.24993 |
| C | -2.23048 | 3.30404 | -0.30489 |
| C | -1.40891 | 4.42502 | -0.20412 |
| C | -0.03775 | 4.25891 | -0.04787 |
| H | 1.57189 | 2.82496 | 0.12691 |
| H | -3.30155 | 3.42953 | -0.43058 |
| H | -1.83929 | 5.41860 | -0.24931 |
| H | 0.61177 | 5.12365 | 0.02602 |
| C | -2.60338 | 0.81627 | -0.42041 |
| H | -3.64603 | 1.15277 | -0.44225 |
| H | -2.41353 | 0.35002 | -1.39121 |
| C | -2.05159 | -1.48016 | 0.27782 |
| C | -0.98240 | -1.64840 | -0.63183 |
| C | -2.66485 | -2.63106 | 0.79983 |
| C | -0.62395 | -2.92374 | -1.06928 |
| C | -2.26125 | -3.89410 | 0.38506 |
| H | -3.47963 | -2.53915 | 1.50612 |
| C | -1.25378 | -4.05380 | -0.56537 |
| H | 0.19290 | -3.01311 | -1.77752 |
| H | -2.75687 | -4.76545 | 0.79804 |
| H | -0.95502 | -5.04190 | -0.89169 |
| N | -2.46401 | -0.20097 | 0.62196 |
| O | 0.30952 | -0.40284 | -2.17462 |
| C | -0.11924 | -0.49968 | -1.04015 |
| C | 0.30989 | 0.47706 | 0.04041 |
| H | 0.06639 | 0.05847 | 1.02029 |
| H | 1.40565 | 0.57707 | -0.04499 |
| C | -3.35617 | -0.01627 | 1.75246 |
| H | -3.34507 | 1.03934 | 2.02891 |
| H | -4.39081 | -0.30367 | 1.52068 |
| H | -3.00819 | -0.59442 | 2.60876 |
| O | 3.45405 | 0.84966 | -0.17901 |
| C | 3.97309 | -0.30491 | 0.35639 |
| C | 3.35462 | -1.56313 | -0.30140 |
| H | 2.27411 | -1.58480 | -0.12589 |
| H | 3.52120 | -1.53178 | -1.38317 |
| H | 3.78080 | -2.49463 | 0.08868 |
| C | 3.68900 | -0.38644 | 1.87435 |
| H | 4.07691 | -1.30425 | 2.33139 |
| H | 4.14663 | 0.47158 | 2.37728 |
| H | 2.60835 | -0.34304 | 2.04380 |
| C | 5.50380 | -0.37993 | 0.15835 |
| H | 5.73731 | -0.35479 | -0.91100 |
| H | 5.97560 | 0.48843 | 0.62923 |
| H | 5.94346 | -1.28828 | 0.58677 |

**TS** of **20** deprotonation to form **56**
47
-981.7162527

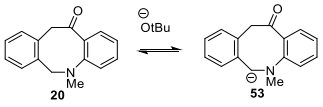
| | | | |
|---|---|---|---|
| C | 0.55625 | 2.99815 | 0.07557 |
| C | -0.22127 | 1.84940 | -0.08300 |
| C | -1.61227 | 1.99847 | -0.26448 |
| C | -2.17661 | 3.27239 | -0.28192 |
| C | -1.38708 | 4.41036 | -0.12198 |
| C | -0.01622 | 4.27003 | 0.05857 |
| H | 1.62632 | 2.87433 | 0.20761 |
| H | -3.24905 | 3.37726 | -0.41917 |
| H | -1.84202 | 5.39409 | -0.13610 |
| H | 0.60898 | 5.14730 | 0.18346 |
| C | -2.50376 | 0.78639 | -0.47623 |
| H | -3.54496 | 1.12352 | -0.53240 |
| H | -2.28304 | 0.32978 | -1.44423 |
| C | -1.93628 | -1.51245 | 0.24550 |
| C | -0.81731 | -1.65911 | -0.61058 |
| C | -2.53028 | -2.67808 | 0.75892 |
| C | -0.38823 | -2.92633 | -0.99310 |
| C | -2.05395 | -3.93496 | 0.40063 |
| H | -3.38473 | -2.60759 | 1.41964 |
| C | -0.99253 | -4.07426 | -0.48934 |
| H | 0.45953 | -2.99956 | -1.66716 |
| H | -2.53617 | -4.81551 | 0.81036 |
| H | -0.63711 | -5.05616 | -0.77625 |
| N | -2.41637 | -0.24549 | 0.55958 |
| O | 0.19192 | -0.27350 | -2.24632 |
| C | -0.05100 | -0.44065 | -1.05015 |
| C | 0.38817 | 0.47428 | 0.00670 |
| H | 0.13751 | 0.05201 | 0.98374 |
| H | 1.72317 | 0.58721 | -0.07039 |
| C | -3.38394 | -0.09651 | 1.62977 |
| H | -3.43611 | 0.95910 | 1.90154 |
| H | -4.39059 | -0.42965 | 1.33951 |
| H | -3.06720 | -0.65619 | 2.51074 |
| O | 3.00095 | 0.79349 | -0.13007 |
| C | 3.70060 | -0.30631 | 0.37529 |
| C | 3.24098 | -1.60787 | -0.30812 |
| H | 2.18537 | -1.79683 | -0.09298 |
| H | 3.35882 | -1.52023 | -1.39255 |
| H | 3.81909 | -2.47168 | 0.03574 |
| C | 3.46744 | -0.43760 | 1.89115 |
| H | 4.00522 | -1.29107 | 2.31685 |
| H | 3.80430 | 0.47234 | 2.39638 |
| H | 2.39986 | -0.56579 | 2.09155 |
| C | 5.19996 | -0.11408 | 0.11708 |
| H | 5.38531 | -0.03277 | -0.95789 |
| H | 5.54455 | 0.80732 | 0.59542 |
| H | 5.78874 | -0.95006 | 0.50907 |

**Product 56**

47

-981.7275513

| | | | |
|---|---|---|---|
| C | -1.38218 | 2.56355 | -0.08239 |
| C | -0.28886 | 1.72115 | 0.13253 |
| C | 0.99252 | 2.30863 | 0.28378 |
| C | 1.12718 | 3.69446 | 0.24659 |
| C | 0.02014 | 4.52053 | 0.04509 |
| C | -1.23592 | 3.95062 | -0.12698 |
| H | -2.36325 | 2.11521 | -0.20669 |
| H | 2.11225 | 4.13790 | 0.36383 |
| H | 0.14398 | 5.59703 | 0.01398 |
| H | -2.10199 | 4.58235 | -0.29214 |
| C | 2.22626 | 1.43984 | 0.50390 |
| H | 3.10374 | 2.09481 | 0.54669 |
| H | 2.15968 | 0.95308 | 1.47882 |
| C | 2.39528 | -0.94356 | -0.23511 |
| C | 1.34893 | -1.45886 | 0.57818 |
| C | 3.31770 | -1.85920 | -0.77161 |
| C | 1.28833 | -2.81713 | 0.85995 |
| C | 3.21436 | -3.22241 | -0.50384 |
| H | 4.13338 | -1.51024 | -1.39192 |
| C | 2.20783 | -3.71558 | 0.31818 |
| H | 0.48362 | -3.17478 | 1.49564 |
| H | 3.94347 | -3.89957 | -0.93541 |
| H | 2.13545 | -4.77560 | 0.52962 |
| N | 2.48340 | 0.42145 | -0.52272 |
| O | 0.28386 | -0.25293 | 2.33664 |
| C | 0.33395 | -0.46749 | 1.09296 |
| C | -0.35100 | 0.23642 | 0.09701 |
| H | -0.18507 | -0.15246 | -0.90712 |
| H | -2.22025 | -0.28485 | 0.57623 |
| C | 3.37945 | 0.85939 | -1.57481 |
| H | 3.13064 | 1.89056 | -1.83173 |
| H | 4.43873 | 0.82520 | -1.27932 |
| H | 3.24686 | 0.24937 | -2.46995 |
| O | -3.16299 | -0.50124 | 0.78211 |
| C | -3.70537 | -1.19642 | -0.34009 |
| C | -2.90551 | -2.47704 | -0.58967 |
| H | -1.86492 | -2.23167 | -0.81960 |
| H | -2.92359 | -3.11027 | 0.30116 |
| H | -3.32507 | -3.04069 | -1.42726 |
| C | -3.65923 | -0.29616 | -1.57673 |
| H | -4.09237 | -0.80249 | -2.44353 |
| H | -4.22161 | 0.62294 | -1.39238 |
| H | -2.62440 | -0.02928 | -1.80888 |
| C | -5.14733 | -1.53021 | 0.02116 |
| H | -5.17611 | -2.15850 | 0.91487 |
| H | -5.70691 | -0.61339 | 0.22255 |
| H | -5.63627 | -2.06441 | -0.79701 |




20 53

**SM 20** + tert-butoxide anion

47

-981.7280946

| | | | |
|---|---|---|---|
| C | 3.91574 | -0.11221 | -1.10856 |
| C | 2.64768 | -0.35110 | -0.58037 |
| C | 2.21140 | 0.40250 | 0.52009 |
| C | 3.06057 | 1.36311 | 1.06702 |
| C | 4.32720 | 1.59433 | 0.53530 |
| C | 4.75579 | 0.85338 | -0.55925 |
| H | 4.24953 | -0.69226 | -1.96264 |
| H | 2.72217 | 1.93935 | 1.92265 |
| H | 4.97230 | 2.34588 | 0.97518 |
| H | 5.73788 | 1.02119 | -0.98585 |
| C | 0.81294 | 0.23377 | 1.07273 |
| H | 0.73780 | 0.78812 | 2.01568 |
| H | 0.08730 | 0.71449 | 0.39989 |
| C | -0.65711 | -1.68425 | 0.64802 |
| C | -0.76790 | -1.47684 | -0.74579 |
| C | -1.67631 | -2.40325 | 1.29609 |
| C | -1.93426 | -1.84876 | -1.41874 |
| C | -2.80578 | -2.80506 | 0.59711 |
| H | -1.60916 | -2.60125 | 2.35792 |
| C | -2.96053 | -2.50690 | -0.75768 |
| H | -1.99670 | -1.65126 | -2.48312 |
| H | -3.58883 | -3.33843 | 1.12456 |
| H | -3.85365 | -2.80847 | -1.29034 |
| N | 0.42595 | -1.15597 | 1.32974 |
| O | 0.20292 | -0.36026 | -2.59061 |
| C | 0.37498 | -0.99158 | -1.56544 |
| C | 1.78457 | -1.43916 | -1.18409 |
| H | 1.72786 | -2.28704 | -0.49935 |
| H | 2.24297 | -1.77343 | -2.11723 |
| C | 0.70871 | -1.61608 | 2.67767 |
| H | 1.72162 | -1.30764 | 2.94122 |
| H | 0.01425 | -1.19389 | 3.41693 |
| H | 0.66117 | -2.70452 | 2.72514 |
| O | -1.01047 | 2.52026 | -0.36242 |
| C | -2.34304 | 2.47556 | -0.03251 |
| C | -2.82133 | 3.82551 | 0.55104 |
| H | -2.24498 | 4.06193 | 1.45138 |
| H | -2.64909 | 4.62108 | -0.18120 |
| H | -3.88571 | 3.82198 | 0.81411 |
| C | -2.62503 | 1.37817 | 1.02136 |
| H | -3.67472 | 1.35769 | 1.33806 |
| H | -2.37174 | 0.39679 | 0.60770 |
| H | -1.99953 | 1.54605 | 1.90487 |
| C | -3.21732 | 2.16120 | -1.26846 |
| H | -3.06702 | 2.93108 | -2.03235 |
| H | -2.91408 | 1.19658 | -1.68945 |
| H | -4.28668 | 2.11376 | -1.03085 |

**TS** of **20** to form **53**

47

-981.7140300

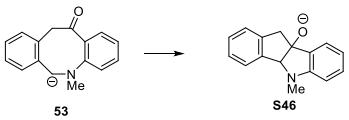
| | | | |
|---|---|---|---|
| C | 3.92765 | -0.82851 | -0.65598 |
| C | 2.60433 | -0.75629 | -0.22571 |
| C | 2.14085 | 0.38675 | 0.45902 |
| C | 3.06056 | 1.42725 | 0.67559 |
| C | 4.37663 | 1.35310 | 0.23250 |
| C | 4.82346 | 0.21636 | -0.43529 |
| H | 4.25958 | -1.71793 | -1.18341 |
| H | 2.72532 | 2.31290 | 1.20819 |
| H | 5.05557 | 2.17843 | 0.41840 |
| H | 5.84732 | 0.14247 | -0.78218 |
| C | 0.71936 | 0.57039 | 0.83659 |
| H | 0.66094 | 1.39300 | 1.56071 |
| H | -0.04542 | 1.17705 | -0.15021 |
| C | -1.00087 | -1.21141 | 0.82489 |
| C | -0.89723 | -1.53363 | -0.54903 |
| C | -2.19207 | -1.56435 | 1.49164 |
| C | -1.98614 | -2.07742 | -1.23309 |
| C | -3.25000 | -2.13616 | 0.79923 |
| H | -2.30536 | -1.34803 | 2.54635 |
| C | -3.16791 | -2.38157 | -0.57283 |
| H | -1.86865 | -2.29873 | -2.28848 |
| H | -4.16056 | -2.37738 | 1.33692 |
| H | -4.00144 | -2.82203 | -1.10566 |
| N | 0.04910 | -0.58153 | 1.45869 |
| O | 0.46693 | -1.22818 | -2.45865 |
| C | 0.40071 | -1.46688 | -1.26531 |
| C | 1.65958 | -1.90022 | -0.51620 |
| H | 1.37835 | -2.41004 | 0.40646 |
| H | 2.15707 | -2.61655 | -1.17487 |
| C | 0.08600 | -0.59915 | 2.91084 |
| H | 1.10489 | -0.37453 | 3.22935 |
| H | -0.58393 | 0.15304 | 3.35345 |
| H | -0.18667 | -1.58316 | 3.29853 |
| O | -0.67320 | 1.91135 | -0.93586 |
| C | -1.90645 | 2.37772 | -0.46549 |
| C | -2.13548 | 3.79880 | -0.99872 |
| H | -1.34101 | 4.46240 | -0.64515 |
| H | -2.11434 | 3.79168 | -2.09232 |
| H | -3.09860 | 4.20506 | -0.67271 |
| C | -1.94565 | 2.41502 | 1.07310 |
| H | -2.90143 | 2.81077 | 1.43010 |
| H | -1.81442 | 1.40843 | 1.48218 |
| H | -1.14287 | 3.05008 | 1.45944 |
| C | -3.04383 | 1.46915 | -0.95778 |
| H | -3.02984 | 1.42000 | -2.05108 |
| H | -2.90395 | 0.45769 | -0.56759 |
| H | -4.02508 | 1.83699 | -0.63891 |

**Product 53** + tert-butanol

47

-981.7207122

| | | | |
|---|---|---|---|
| C | 4.06524 | -0.63097 | -0.62269 |
| C | 2.73889 | -0.63938 | -0.21008 |
| C | 2.17221 | 0.48393 | 0.45406 |
| C | 3.02573 | 1.60291 | 0.63063 |
| C | 4.34378 | 1.60425 | 0.19531 |
| C | 4.89013 | 0.47994 | -0.42560 |
| H | 4.45759 | -1.50627 | -1.13386 |
| H | 2.62723 | 2.48175 | 1.13039 |
| H | 4.95684 | 2.48573 | 0.35655 |
| H | 5.91976 | 0.47144 | -0.76226 |
| C | 0.77921 | 0.54337 | 0.81448 |
| H | 0.54551 | 1.44459 | 1.39149 |
| H | -0.45776 | 1.43762 | -0.47184 |
| C | -0.86287 | -1.30285 | 0.81642 |
| C | -0.73698 | -1.57530 | -0.56675 |
| C | -2.02179 | -1.76524 | 1.47199 |
| C | -1.77622 | -2.18488 | -1.26862 |
| C | -3.03440 | -2.39500 | 0.75831 |
| H | -2.15349 | -1.58875 | 2.53181 |
| C | -2.93350 | -2.59634 | -0.61882 |
| H | -1.64129 | -2.36687 | -2.32968 |
| H | -3.92587 | -2.71601 | 1.28645 |
| H | -3.73199 | -3.08263 | -1.16554 |
| N | 0.14024 | -0.60409 | 1.45135 |
| O | 0.61285 | -1.03820 | -2.43804 |
| C | 0.55748 | -1.36136 | -1.26172 |
| C | 1.83444 | -1.80080 | -0.53797 |
| H | 1.56113 | -2.35952 | 0.35932 |
| H | 2.34439 | -2.47928 | -1.22801 |
| C | 0.14090 | -0.58437 | 2.90619 |
| H | 1.13387 | -0.28506 | 3.24124 |
| H | -0.58754 | 0.13394 | 3.31145 |
| H | -0.07951 | -1.57294 | 3.31694 |
| O | -0.98972 | 2.08899 | -0.99877 |
| C | -2.27219 | 2.29091 | -0.40489 |
| C | -2.74861 | 3.66158 | -0.87546 |
| H | -2.06285 | 4.43874 | -0.52932 |
| H | -2.78517 | 3.69138 | -1.96738 |
| H | -3.74740 | 3.87773 | -0.48855 |
| C | -2.17041 | 2.26034 | 1.12107 |
| H | -3.14409 | 2.47471 | 1.56958 |
| H | -1.84271 | 1.27375 | 1.46217 |
| H | -1.45263 | 3.00642 | 1.47261 |
| C | -3.23706 | 1.20350 | -0.87922 |
| H | -3.28924 | 1.19989 | -1.97137 |
| H | -2.89326 | 0.22216 | -0.54418 |
| H | -4.24215 | 1.37434 | -0.48274 |




53 S46

**SM 53**

32

-748.0665397

| | | | |
|---|---|---|---|
| C | 3.10061 | -0.99463 | 0.91698 |
| C | 1.86670 | -0.46060 | 0.57690 |
| C | 1.75868 | 0.60213 | -0.37665 |
| C | 2.98496 | 1.02461 | -0.97116 |
| C | 4.20567 | 0.46628 | -0.62747 |
| C | 4.29199 | -0.54226 | 0.33760 |
| H | 3.13149 | -1.81316 | 1.63221 |
| H | 2.95038 | 1.82143 | -1.70942 |
| H | 5.10885 | 0.83132 | -1.10800 |
| H | 5.24447 | -0.97927 | 0.61081 |
| C | 0.50763 | 1.12326 | -0.79475 |
| H | 0.56111 | 1.92227 | -1.53973 |
| C | -1.74320 | 0.62787 | 0.07323 |
| C | -1.65844 | -0.76410 | -0.16426 |
| C | -3.02497 | 1.19146 | 0.22353 |
| C | -2.81161 | -1.52158 | -0.36011 |
| C | -4.16369 | 0.41236 | 0.05111 |
| H | -3.13533 | 2.24877 | 0.42579 |
| C | -4.07246 | -0.94346 | -0.26210 |
| H | -2.70309 | -2.58453 | -0.54838 |
| H | -5.13806 | 0.87962 | 0.14647 |
| H | -4.96614 | -1.53877 | -0.40205 |
| N | -0.57550 | 1.35872 | 0.14155 |
| O | -0.09447 | -2.44763 | -0.73952 |
| C | -0.35084 | -1.46302 | -0.06378 |
| C | 0.58725 | -1.07451 | 1.08648 |
| H | 0.05710 | -0.40768 | 1.76907 |
| H | 0.81046 | -2.00692 | 1.61337 |
| C | -0.66447 | 2.72391 | 0.64001 |
| H | 0.33957 | 3.05461 | 0.90311 |
| H | -1.06721 | 3.41595 | -0.11440 |
| H | -1.29218 | 2.77990 | 1.53319 |

**TS 53** cyclising to form **S46**

32

-748.0659566

| | | | |
|---|---|---|---|
| C | 3.10118 | -0.99582 | 1.00100 |
| C | 1.86825 | -0.52209 | 0.57842 |
| C | 1.77100 | 0.52389 | -0.38099 |
| C | 2.98890 | 1.00403 | -0.92032 |
| C | 4.21901 | 0.50521 | -0.50551 |
| C | 4.29386 | -0.48571 | 0.47392 |
| H | 3.13565 | -1.80805 | 1.72243 |
| H | 2.95307 | 1.79213 | -1.66755 |
| H | 5.13056 | 0.90377 | -0.94034 |
| H | 5.25128 | -0.87388 | 0.80049 |
| C | 0.47942 | 0.93435 | -0.85708 |
| H | 0.52132 | 1.64244 | -1.69369 |
| C | -1.74516 | 0.64300 | 0.09035 |
| C | -1.68915 | -0.74194 | -0.18697 |
| C | -3.00149 | 1.22296 | 0.33472 |
| C | -2.85493 | -1.48617 | -0.31429 |
| C | -4.15948 | 0.45420 | 0.22402 |
| H | -3.08607 | 2.27701 | 0.56518 |
| C | -4.10303 | -0.89441 | -0.11734 |
| H | -2.77237 | -2.54535 | -0.53579 |
| H | -5.12089 | 0.92854 | 0.39008 |
| H | -5.01099 | -1.47793 | -0.20838 |
| N | -0.55141 | 1.33180 | 0.08602 |
| O | -0.12445 | -2.36596 | -0.95089 |
| C | -0.35557 | -1.40594 | -0.21868 |
| C | 0.56773 | -1.15122 | 0.99141 |
| H | 0.03408 | -0.52553 | 1.71064 |
| H | 0.74450 | -2.12877 | 1.45075 |
| C | -0.58050 | 2.74221 | 0.44110 |
| H | 0.44542 | 3.07931 | 0.58475 |
| H | -1.04033 | 3.35628 | -0.34787 |
| H | -1.13007 | 2.90580 | 1.37180 |

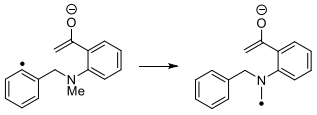
**Product S46**

32

-748.1071091

| | | | |
|---|---|---|---|
| C | -3.11162 | -1.14171 | -1.05056 |
| C | -1.87630 | -0.82133 | -0.50129 |
| C | -1.75125 | 0.29425 | 0.33635 |
| C | -2.85359 | 1.08051 | 0.64450 |
| C | -4.09472 | 0.75847 | 0.08926 |
| C | -4.21993 | -0.34315 | -0.75395 |
| H | -3.22136 | -2.00817 | -1.69483 |
| H | -2.75840 | 1.92801 | 1.31619 |
| H | -4.96515 | 1.36110 | 0.32268 |
| H | -5.18868 | -0.59057 | -1.17356 |
| C | -0.32928 | 0.41932 | 0.80449 |
| H | -0.23703 | 0.73939 | 1.85335 |
| C | 1.74961 | 0.69497 | -0.17514 |
| C | 1.70254 | -0.66105 | 0.18629 |
| C | 2.94351 | 1.28894 | -0.57869 |
| C | 2.84572 | -1.43210 | 0.13850 |
| C | 4.09243 | 0.48984 | -0.63475 |
| H | 2.99571 | 2.34041 | -0.83627 |
| C | 4.05399 | -0.85520 | -0.28233 |
| H | 2.80613 | -2.47451 | 0.44020 |
| H | 5.03035 | 0.93714 | -0.94554 |
| H | 4.95887 | -1.45073 | -0.32040 |
| N | 0.48708 | 1.28222 | -0.06818 |
| O | 0.15025 | -1.85221 | 1.66525 |
| C | 0.27910 | -1.03062 | 0.60717 |
| C | -0.54859 | -1.51862 | -0.64992 |
| H | -0.07840 | -1.21271 | -1.59237 |
| H | -0.62440 | -2.60797 | -0.64088 |
| C | 0.38767 | 2.71231 | 0.13429 |
| H | -0.66474 | 3.00049 | 0.12680 |
| H | 0.83317 | 3.02517 | 1.09091 |
| H | 0.88663 | 3.24611 | -0.67620 |

## 9 Cyclisation of 18 in Benzene Scheme S4.1



51 54

**SM 51**

33

-748.5611009

| | | | |
|---|---|---|---|
| C | -4.12495 | 1.20792 | 0.75190 |
| C | -2.80403 | 1.03867 | 0.42030 |
| C | -2.28731 | 0.04678 | -0.38833 |
| C | -3.22410 | -0.85696 | -0.90232 |
| C | -4.58263 | -0.73085 | -0.61096 |
| C | -5.03926 | 0.29364 | 0.21215 |
| H | -4.45552 | 2.01119 | 1.40103 |
| H | -2.87579 | -1.67111 | -1.53056 |
| H | -5.28635 | -1.44613 | -1.02110 |
| H | -6.09512 | 0.38416 | 0.44193 |
| C | -0.81548 | -0.05505 | -0.71638 |
| H | -0.58759 | -1.03371 | -1.16085 |
| H | -0.57215 | 0.71176 | -1.45798 |
| C | 1.34103 | 0.62811 | 0.14480 |
| C | 2.45512 | -0.21642 | -0.01866 |
| C | 1.50005 | 2.01162 | 0.01626 |
| C | 3.69995 | 0.37631 | -0.26140 |
| C | 2.73820 | 2.57884 | -0.25949 |
| H | 0.62321 | 2.63531 | 0.16005 |
| C | 3.85169 | 1.75314 | -0.38497 |
| H | 4.55590 | -0.27820 | -0.38582 |
| H | 2.83440 | 3.65480 | -0.35590 |
| H | 4.82924 | 2.17695 | -0.58804 |
| N | 0.01840 | 0.17777 | 0.45936 |
| O | 1.46120 | -2.18746 | -0.87557 |
| C | 2.33092 | -1.73301 | -0.05824 |
| C | 3.16613 | -2.44363 | 0.76816 |
| H | 3.85816 | -1.94058 | 1.43171 |
| H | 3.13481 | -3.52768 | 0.76897 |
| C | -0.10078 | -0.89213 | 1.44561 |
| H | -1.09967 | -0.84379 | 1.88971 |
| H | 0.05604 | -1.88561 | 1.01054 |
| H | 0.63475 | -0.73396 | 2.23486 |

**TS** of **51** to form **54**

33

-748.5452234

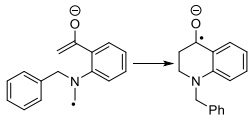
| | | | |
|---|---|---|---|
| C | 3.34033 | -0.81390 | -1.44741 |
| C | 2.25745 | -0.96373 | -0.59699 |
| C | 2.18732 | -0.32401 | 0.62741 |
| C | 3.24702 | 0.49966 | 1.01633 |
| C | 4.34897 | 0.66105 | 0.17892 |
| C | 4.39903 | 0.00796 | -1.05076 |
| H | 3.37554 | -1.31747 | -2.40817 |
| H | 3.20741 | 1.02079 | 1.96943 |
| H | 5.16714 | 1.30404 | 0.48320 |
| H | 5.25636 | 0.14161 | -1.70214 |
| C | 0.96831 | -0.54255 | 1.52511 |
| H | 1.13657 | -1.44457 | 2.12519 |
| H | 0.84295 | 0.29072 | 2.21776 |
| C | -0.97401 | 0.37516 | 0.31064 |
| C | -2.30743 | 0.22803 | -0.12619 |
| C | -0.39229 | 1.65209 | 0.31823 |
| C | -2.99124 | 1.36134 | -0.56053 |
| C | -1.10993 | 2.76979 | -0.09377 |
| H | 0.63816 | 1.77779 | 0.62575 |
| C | -2.41722 | 2.62931 | -0.54314 |
| H | -4.01338 | 1.23157 | -0.90152 |
| H | -0.63469 | 3.74425 | -0.07455 |
| H | -2.98433 | 3.49326 | -0.87067 |
| N | -0.25170 | -0.75150 | 0.77111 |
| O | -3.12909 | -1.64034 | -1.33230 |
| C | -3.06070 | -1.09964 | -0.17627 |
| C | -3.59844 | -1.53956 | 1.00365 |
| H | -4.16392 | -2.46495 | 1.03251 |
| H | -3.45926 | -0.97973 | 1.92017 |
| C | -0.15428 | -1.88966 | -0.07865 |
| H | -0.96707 | -1.97348 | -0.79635 |
| H | 0.01505 | -2.80799 | 0.48923 |
| H | 0.92063 | -1.70065 | -0.68866 |

**Product 54**

33

-748.5921792

| | | | |
|---|---|---|---|
| C | -3.51057 | 0.40350 | 1.49075 |
| C | -2.30458 | 0.04181 | 0.89484 |
| C | -2.27767 | -0.40319 | -0.42478 |
| C | -3.47621 | -0.48546 | -1.13595 |
| C | -4.68115 | -0.12426 | -0.54354 |
| C | -4.70126 | 0.32324 | 0.77536 |
| H | -3.51770 | 0.74749 | 2.51877 |
| H | -3.46258 | -0.83712 | -2.16365 |
| H | -5.60372 | -0.19246 | -1.10897 |
| H | -5.63833 | 0.60429 | 1.24182 |
| C | -0.98027 | -0.78307 | -1.12126 |
| H | -1.10120 | -1.77856 | -1.56348 |
| H | -0.79705 | -0.09135 | -1.94741 |
| C | 1.03852 | 0.30931 | -0.20191 |
| C | 2.42051 | 0.18675 | 0.05332 |
| C | 0.48659 | 1.58838 | -0.39726 |
| C | 3.17942 | 1.35300 | 0.14274 |
| C | 1.27618 | 2.72875 | -0.33347 |
| H | -0.57709 | 1.69346 | -0.57800 |
| C | 2.63375 | 2.61870 | -0.05063 |
| H | 4.24021 | 1.24407 | 0.34537 |
| H | 0.82167 | 3.70107 | -0.48918 |
| H | 3.25920 | 3.50205 | 0.00871 |
| N | 0.19455 | -0.81636 | -0.27571 |
| O | 3.39920 | -1.47790 | 1.43568 |
| C | 3.16812 | -1.13353 | 0.22893 |
| C | 3.53589 | -1.77005 | -0.92789 |
| H | 4.08580 | -2.70423 | -0.88455 |
| H | 3.27596 | -1.35766 | -1.89500 |
| C | 0.33146 | -1.90985 | 0.55607 |
| H | 1.17212 | -1.93704 | 1.23240 |
| H | -0.16809 | -2.81657 | 0.24179 |
| H | -1.37707 | 0.09597 | 1.45396 |




54 S47

**TS** of **54** cyclising to form **S47**

33

-748.5797844

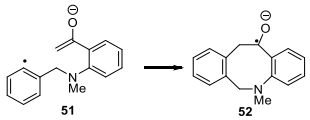
| | | | |
|---|---|---|---|
| C | -3.39545 | 0.45421 | 1.57517 |
| C | -2.22702 | 0.07908 | 0.91627 |
| C | -2.27507 | -0.37390 | -0.40016 |
| C | -3.51025 | -0.44636 | -1.04619 |
| C | -4.67854 | -0.07150 | -0.39108 |
| C | -4.62376 | 0.38085 | 0.92545 |
| H | -3.34436 | 0.80497 | 2.59971 |
| H | -3.55544 | -0.80275 | -2.07146 |
| H | -5.63090 | -0.13406 | -0.90564 |
| H | -5.53203 | 0.67186 | 1.44038 |
| C | -1.01120 | -0.77312 | -1.14660 |
| H | -1.15545 | -1.77514 | -1.56677 |
| H | -0.86600 | -0.09875 | -1.99601 |
| C | 1.04583 | 0.30716 | -0.31931 |
| C | 2.41796 | 0.17737 | 0.03889 |
| C | 0.53640 | 1.59591 | -0.58751 |
| C | 3.17516 | 1.34103 | 0.18904 |
| C | 1.33664 | 2.72313 | -0.48527 |
| H | -0.51254 | 1.71732 | -0.83442 |
| C | 2.66708 | 2.60631 | -0.07563 |
| H | 4.20651 | 1.21107 | 0.49964 |
| H | 0.91003 | 3.69764 | -0.69797 |
| H | 3.29259 | 3.48539 | 0.02769 |
| N | 0.18777 | -0.79084 | -0.34267 |
| O | 4.00555 | -1.21398 | 1.14112 |
| C | 3.11486 | -1.14421 | 0.23677 |
| C | 2.65159 | -2.20857 | -0.53731 |
| H | 3.12074 | -3.17928 | -0.40988 |
| H | 2.10666 | -2.02981 | -1.45480 |
| C | 0.47884 | -1.95476 | 0.38070 |
| H | 0.83835 | -1.82465 | 1.39548 |
| H | -0.18868 | -2.78531 | 0.18648 |
| H | -1.26676 | 0.13362 | 1.41777 |

**Product S47**

33

-748.6544530

| | | | |
|---|---|---|---|
| C | -3.00664 | 0.50616 | 1.66388 |
| C | -1.94208 | 0.16355 | 0.83277 |
| C | -2.17485 | -0.28274 | -0.46735 |
| C | -3.49420 | -0.37992 | -0.91604 |
| C | -4.55887 | -0.03465 | -0.09066 |
| C | -4.31724 | 0.41064 | 1.20670 |
| H | -2.80769 | 0.85286 | 2.67163 |
| H | -3.68671 | -0.73314 | -1.92534 |
| H | -5.57592 | -0.11665 | -0.45755 |
| H | -5.14361 | 0.67934 | 1.85458 |
| C | -1.04349 | -0.67156 | -1.41236 |
| H | -1.30734 | -1.62982 | -1.87262 |
| H | -0.99768 | 0.05356 | -2.23121 |
| C | 1.02815 | 0.33451 | -0.52645 |
| C | 2.30933 | 0.13671 | 0.11264 |
| C | 0.59372 | 1.61658 | -0.82483 |
| C | 3.07793 | 1.30733 | 0.40205 |
| C | 1.38654 | 2.75191 | -0.53926 |
| H | -0.38572 | 1.76927 | -1.26329 |
| C | 2.62778 | 2.57553 | 0.08009 |
| H | 4.04261 | 1.15935 | 0.87310 |
| H | 1.01988 | 3.74055 | -0.78804 |
| H | 3.24467 | 3.43899 | 0.31154 |
| N | 0.27215 | -0.81076 | -0.84164 |
| O | 3.96309 | -1.37010 | 0.91681 |
| C | 2.82485 | -1.15929 | 0.40186 |
| C | 1.95737 | -2.35003 | 0.03460 |
| H | 2.13138 | -3.14163 | 0.77002 |
| H | 2.26162 | -2.74116 | -0.94558 |
| C | 0.48261 | -1.98253 | 0.00121 |
| H | 0.12830 | -1.80637 | 1.02889 |
| H | -0.11546 | -2.79991 | -0.41251 |
| H | -0.92351 | 0.25757 | 1.19028 |

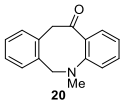



**Product 52** after $S_{RN}1$ cyclisation

33

-748.6424854

| | | | |
|---|---|---|---|
| C | 3.12564 | -1.10191 | 0.68063 |
| C | 1.86789 | -0.54916 | 0.43315 |
| C | 1.79132 | 0.58175 | -0.39931 |
| C | 2.95654 | 1.13288 | -0.92694 |
| C | 4.20609 | 0.57349 | -0.66600 |
| C | 4.28760 | -0.55542 | 0.13873 |
| H | 3.19055 | -1.98323 | 1.31098 |
| H | 2.88266 | 2.01231 | -1.56041 |
| H | 5.10122 | 1.01435 | -1.08993 |
| H | 5.24915 | -1.01148 | 0.34727 |
| C | 0.44751 | 1.15388 | -0.78801 |
| H | 0.59449 | 2.12370 | -1.28312 |
| H | -0.00731 | 0.48744 | -1.52517 |
| C | -1.71329 | 0.62449 | 0.18602 |
| C | -1.65549 | -0.79872 | -0.05164 |
| C | -2.93199 | 1.28447 | 0.20093 |
| C | -2.87241 | -1.41417 | -0.48072 |
| C | -4.13708 | 0.61028 | -0.08064 |
| H | -2.95815 | 2.35221 | 0.39024 |
| C | -4.07644 | -0.73496 | -0.46765 |
| H | -2.82976 | -2.46390 | -0.74626 |
| H | -5.07960 | 1.14379 | -0.05244 |
| H | -4.98676 | -1.25797 | -0.74559 |
| N | -0.48195 | 1.31294 | 0.33209 |
| O | -0.39383 | -2.78151 | -0.35361 |
| C | -0.48562 | -1.60943 | 0.12248 |
| C | 0.63670 | -1.16064 | 1.06936 |
| H | 0.24609 | -0.46195 | 1.81167 |
| H | 0.94665 | -2.07161 | 1.58858 |
| C | -0.50282 | 2.65432 | 0.86484 |
| H | 0.52314 | 2.95987 | 1.08718 |
| H | -0.93483 | 3.39294 | 0.16750 |
| H | -1.07826 | 2.67812 | 1.79235 |



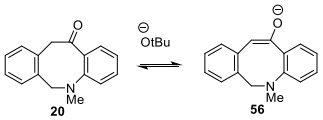
20

**Product 20**

33

-748.5933166

| | | | |
|---|---|---|---|
| C | 3.07550 | -1.11816 | 0.84233 |
| C | 1.84290 | -0.61645 | 0.42964 |
| C | 1.81484 | 0.49160 | -0.42962 |
| C | 3.01047 | 1.07408 | -0.84090 |
| C | 4.23754 | 0.56945 | -0.41871 |
| C | 4.26820 | -0.53258 | 0.42564 |
| H | 3.10127 | -1.98087 | 1.49946 |
| H | 2.97946 | 1.93380 | -1.50290 |
| H | 5.15895 | 1.03471 | -0.74811 |
| H | 5.21497 | -0.93895 | 0.76153 |
| C | 0.49697 | 1.02689 | -0.94376 |
| H | 0.67883 | 1.94395 | -1.51668 |
| H | 0.05936 | 0.30999 | -1.64361 |
| C | -1.70057 | 0.65194 | 0.08880 |
| C | -1.72729 | -0.74107 | -0.13886 |
| C | -2.91957 | 1.32042 | 0.27856 |
| C | -2.94576 | -1.40542 | -0.28117 |
| C | -4.12079 | 0.63008 | 0.18251 |
| H | -2.93091 | 2.38613 | 0.46627 |
| C | -4.14709 | -0.73024 | -0.11888 |
| H | -2.92738 | -2.47151 | -0.47764 |
| H | -5.05060 | 1.16925 | 0.32386 |
| H | -5.08919 | -1.25601 | -0.20802 |
| N | -0.47826 | 1.31310 | 0.10789 |
| O | -0.35624 | -2.54848 | -0.80925 |
| C | -0.48541 | -1.57112 | -0.10513 |
| C | 0.56839 | -1.24541 | 0.95474 |
| H | 0.13054 | -0.59497 | 1.71492 |
| H | 0.81484 | -2.20396 | 1.41616 |
| C | -0.40609 | 2.66544 | 0.62788 |
| H | 0.64247 | 2.90783 | 0.80951 |
| H | -0.81896 | 3.40660 | -0.07083 |
| H | -0.93927 | 2.73349 | 1.57651 |



20 56

**Opt SM 20** + tert-butoxide anion

47

-981.6838637

| | | | |
|---|---|---|---|
| C | 1.39365 | 2.42079 | 0.00428 |
| C | 0.22650 | 1.66292 | -0.10495 |
| C | -1.00293 | 2.30890 | -0.29851 |
| C | -1.04827 | 3.69979 | -0.36423 |
| C | 0.11598 | 4.45556 | -0.24797 |
| C | 1.33532 | 3.81179 | -0.06653 |
| H | 2.33335 | 1.88633 | 0.14327 |
| H | -2.00436 | 4.19403 | -0.51160 |
| H | 0.06798 | 5.53754 | -0.30044 |
| H | 2.24787 | 4.39143 | 0.01897 |
| C | -2.26945 | 1.50069 | -0.47784 |
| H | -3.12664 | 2.18218 | -0.54693 |
| H | -2.23045 | 0.96000 | -1.42718 |
| C | -2.59567 | -0.81699 | 0.29852 |
| C | -1.64102 | -1.39068 | -0.57093 |
| C | -3.59185 | -1.64837 | 0.83492 |
| C | -1.75641 | -2.72439 | -0.95317 |
| C | -3.66110 | -2.98914 | 0.47517 |
| H | -4.33133 | -1.23982 | 1.51197 |
| C | -2.75963 | -3.53484 | -0.43504 |
| H | -1.01314 | -3.12480 | -1.63412 |
| H | -4.44350 | -3.60848 | 0.89974 |
| H | -2.82609 | -4.57742 | -0.71999 |
| N | -2.52671 | 0.53766 | 0.59323 |
| O | -0.00018 | -0.74706 | -2.14357 |
| C | -0.41703 | -0.63721 | -1.00934 |
| C | 0.32728 | 0.15969 | 0.04260 |
| H | -0.04141 | -0.12266 | 1.03249 |
| H | 1.39843 | -0.10321 | -0.01313 |
| C | -3.28306 | 1.07157 | 1.70596 |
| H | -2.88186 | 2.05690 | 1.95106 |
| H | -4.35414 | 1.17928 | 1.47782 |
| H | -3.16977 | 0.43259 | 2.58269 |
| O | 3.36979 | 0.06570 | 0.36274 |
| C | 3.98735 | -1.15099 | 0.37774 |
| C | 2.96890 | -2.29915 | 0.15497 |
| H | 2.20885 | -2.26701 | 0.94344 |
| H | 2.46614 | -2.15565 | -0.80759 |
| H | 3.43635 | -3.29150 | 0.16165 |
| C | 4.69241 | -1.40454 | 1.73272 |
| H | 5.19066 | -2.38113 | 1.78283 |
| H | 5.43820 | -0.62132 | 1.90096 |
| H | 3.95264 | -1.34552 | 2.53728 |
| C | 5.05639 | -1.24985 | -0.73741 |
| H | 4.57651 | -1.09237 | -1.70824 |
| H | 5.79803 | -0.45786 | -0.59354 |
| H | 5.57396 | -2.21760 | -0.75317 |

**TS 20** deprotonation to form **56**

47

-981.6767959

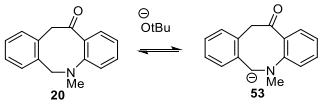
| | | | |
|---|---|---|---|
| C | 0.86660 | 2.86018 | 0.26028 |
| C | -0.03663 | 1.82231 | 0.02159 |
| C | -1.36828 | 2.14932 | -0.30589 |
| C | -1.75747 | 3.48496 | -0.38233 |
| C | -0.84636 | 4.51154 | -0.13941 |
| C | 0.46825 | 4.19389 | 0.18247 |
| H | 1.89193 | 2.59321 | 0.49728 |
| H | -2.78690 | 3.72585 | -0.63439 |
| H | -1.16370 | 5.54655 | -0.20163 |
| H | 1.18818 | 4.98365 | 0.36863 |
| C | -2.37784 | 1.05729 | -0.61417 |
| H | -3.35503 | 1.52234 | -0.79497 |
| H | -2.10395 | 0.55514 | -1.54491 |
| C | -2.20090 | -1.28234 | 0.19912 |
| C | -1.01892 | -1.59759 | -0.51297 |
| C | -2.99536 | -2.34237 | 0.66512 |
| C | -0.70637 | -2.92053 | -0.79804 |
| C | -2.64018 | -3.66286 | 0.40589 |
| H | -3.90670 | -2.13675 | 1.21242 |
| C | -1.50427 | -3.96527 | -0.33759 |
| H | 0.20157 | -3.12130 | -1.35787 |
| H | -3.27377 | -4.46068 | 0.77793 |
| H | -1.23865 | -4.99476 | -0.54537 |
| N | -2.54461 | 0.04617 | 0.43200 |
| O | 0.29084 | -0.39352 | -2.07287 |
| C | -0.06645 | -0.49363 | -0.90341 |
| C | 0.37929 | 0.38526 | 0.18133 |
| H | -0.01287 | 0.01987 | 1.13503 |
| H | 1.70162 | 0.35647 | 0.26586 |
| C | -3.56010 | 0.36110 | 1.41183 |
| H | -3.48010 | 1.42118 | 1.66086 |
| H | -4.58123 | 0.16708 | 1.04807 |
| H | -3.39839 | -0.21211 | 2.32630 |
| O | 2.98431 | 0.50227 | 0.44515 |
| C | 3.74017 | -0.65749 | 0.33337 |
| C | 2.86960 | -1.86749 | -0.06263 |
| H | 2.07527 | -2.02296 | 0.67510 |
| H | 2.40057 | -1.68891 | -1.03469 |
| H | 3.46786 | -2.78273 | -0.12478 |
| C | 4.42409 | -0.96267 | 1.67821 |
| H | 5.05729 | -1.85615 | 1.63025 |
| H | 5.04188 | -0.10930 | 1.97236 |
| H | 3.66281 | -1.11323 | 2.44910 |
| C | 4.82459 | -0.46752 | -0.74173 |
| H | 4.34828 | -0.25593 | -1.70300 |
| H | 5.45339 | 0.38724 | -0.47631 |
| H | 5.46100 | -1.35352 | -0.84966 |

**Product 56**

47

-981.6884259

| | | | |
|---|---|---|---|
| C | -1.02221 | 2.78710 | -0.05615 |
| C | -0.06252 | 1.79660 | 0.17277 |
| C | 1.29299 | 2.19589 | 0.28381 |
| C | 1.62986 | 3.54387 | 0.19267 |
| C | 0.65493 | 4.51860 | -0.02396 |
| C | -0.67410 | 4.13373 | -0.15515 |
| H | -2.06117 | 2.48330 | -0.13982 |
| H | 2.67249 | 3.83895 | 0.27928 |
| H | 0.93537 | 5.56360 | -0.09549 |
| H | -1.44247 | 4.88071 | -0.32516 |
| C | 2.39132 | 1.16322 | 0.50266 |
| H | 3.35555 | 1.68623 | 0.52360 |
| H | 2.27053 | 0.70039 | 1.48344 |
| C | 2.19782 | -1.22696 | -0.23059 |
| C | 1.10627 | -1.58146 | 0.60670 |
| C | 2.95848 | -2.26441 | -0.79448 |
| C | 0.84700 | -2.91552 | 0.88241 |
| C | 2.65514 | -3.59923 | -0.53271 |
| H | 3.80356 | -2.03317 | -1.43091 |
| C | 1.60540 | -3.93847 | 0.31145 |
| H | 0.01387 | -3.14848 | 1.53851 |
| H | 3.26137 | -4.37574 | -0.98702 |
| H | 1.37683 | -4.97732 | 0.51904 |
| N | 2.48124 | 0.11103 | -0.51676 |
| O | 0.32874 | -0.21794 | 2.38809 |
| C | 0.27231 | -0.44594 | 1.15774 |
| C | -0.35785 | 0.34195 | 0.17908 |
| H | -0.29594 | -0.07957 | -0.82474 |
| H | -2.29723 | 0.06506 | 0.64365 |
| C | 3.35843 | 0.42609 | -1.62130 |
| H | 3.22890 | 1.48044 | -1.87424 |
| H | 4.42287 | 0.25593 | -1.39256 |
| H | 3.09410 | -0.16458 | -2.50083 |
| O | -3.27304 | -0.05610 | 0.75636 |
| C | -3.75386 | -0.81227 | -0.34481 |
| C | -3.01181 | -2.14949 | -0.42905 |
| H | -1.94608 | -1.98223 | -0.60454 |
| H | -3.12191 | -2.69146 | 0.51377 |
| H | -3.40922 | -2.76781 | -1.23945 |
| C | -3.56787 | -0.01917 | -1.64200 |
| H | -3.95247 | -0.57487 | -2.50253 |
| H | -4.09942 | 0.93377 | -1.57319 |
| H | -2.50741 | 0.18940 | -1.80403 |
| C | -5.23698 | -1.04743 | -0.07909 |
| H | -5.36488 | -1.60316 | 0.85291 |
| H | -5.75431 | -0.08957 | 0.01639 |
| H | -5.69380 | -1.61489 | -0.89440 |




**SM 20** + tert-butoxide anion
47
-981.6817071

| | | | |
|---|---|---|---|
| C | 4.13108 | -0.45909 | -0.59342 |
| C | 2.78165 | -0.48545 | -0.24370 |
| C | 2.19546 | 0.65835 | 0.31801 |
| C | 2.98288 | 1.79142 | 0.51834 |
| C | 4.32993 | 1.81075 | 0.16853 |
| C | 4.90827 | 0.67797 | -0.39059 |
| H | 4.57752 | -1.34336 | -1.03668 |
| H | 2.52377 | 2.67626 | 0.94772 |
| H | 4.91957 | 2.70573 | 0.33081 |
| H | 5.95503 | 0.67661 | -0.67259 |
| C | 0.72223 | 0.71125 | 0.64422 |
| H | 0.52478 | 1.61595 | 1.22926 |
| H | 0.09601 | 0.86161 | -0.25513 |
| C | -0.74433 | -1.25524 | 0.86587 |
| C | -0.60412 | -1.71247 | -0.46327 |
| C | -1.88174 | -1.65803 | 1.58756 |
| C | -1.62906 | -2.44241 | -1.06575 |
| C | -2.86709 | -2.42581 | 0.98310 |
| H | -2.01834 | -1.32543 | 2.60852 |
| C | -2.76214 | -2.80761 | -0.35347 |
| H | -1.49576 | -2.74801 | -2.09740 |
| H | -3.74384 | -2.70388 | 1.55789 |
| H | -3.54666 | -3.38547 | -0.82584 |
| N | 0.22988 | -0.43747 | 1.41622 |
| O | 0.69600 | -1.49564 | -2.42928 |
| C | 0.67332 | -1.58055 | -1.22054 |
| C | 1.98541 | -1.75502 | -0.45072 |
| H | 1.77924 | -2.22010 | 0.51544 |
| H | 2.57871 | -2.44560 | -1.05404 |
| C | 0.25303 | -0.23969 | 2.85196 |
| H | 1.22011 | 0.18852 | 3.12246 |
| H | -0.53564 | 0.44732 | 3.19226 |
| H | 0.14454 | -1.19365 | 3.37129 |
| O | -1.27455 | 2.02148 | -1.14155 |
| C | -2.49144 | 2.18578 | -0.55595 |
| C | -3.14081 | 3.52876 | -0.97556 |
| H | -2.48054 | 4.35303 | -0.68736 |
| H | -3.24804 | 3.54714 | -2.06456 |
| H | -4.12704 | 3.69214 | -0.52146 |
| C | -2.38080 | 2.18530 | 0.99349 |
| H | -3.34675 | 2.33247 | 1.49360 |
| H | -1.96373 | 1.22706 | 1.32188 |
| H | -1.69810 | 2.98278 | 1.30665 |
| C | -3.46538 | 1.04595 | -0.94636 |
| H | -3.56964 | 1.02307 | -2.03580 |
| H | -3.04230 | 0.08850 | -0.62608 |
| H | -4.46175 | 1.15797 | -0.49831 |

**TS 20** deprotonation to form **53**
47
-981.6749539

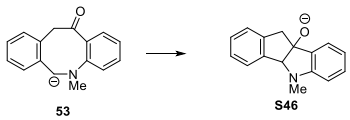
| | | | |
|---|---|---|---|
| C | 3.93132 | -0.81603 | -0.66124 |
| C | 2.60841 | -0.74051 | -0.23165 |
| C | 2.15177 | 0.40405 | 0.45211 |
| C | 3.07230 | 1.44148 | 0.66803 |
| C | 4.38816 | 1.36283 | 0.22752 |
| C | 4.83070 | 0.22441 | -0.43892 |
| H | 4.25834 | -1.70407 | -1.19397 |
| H | 2.73404 | 2.33141 | 1.19073 |
| H | 5.06855 | 2.18799 | 0.40939 |
| H | 5.85362 | 0.14796 | -0.78866 |
| C | 0.73043 | 0.59008 | 0.83397 |
| H | 0.67109 | 1.41582 | 1.55429 |
| H | -0.01916 | 1.13528 | -0.12739 |
| C | -0.98897 | -1.19074 | 0.83474 |
| C | -0.89614 | -1.51909 | -0.53800 |
| C | -2.17428 | -1.53716 | 1.51327 |
| C | -1.99160 | -2.06312 | -1.20690 |
| C | -3.23922 | -2.11396 | 0.83498 |
| H | -2.27860 | -1.30872 | 2.56641 |
| C | -3.16833 | -2.36487 | -0.53485 |
| H | -1.88230 | -2.27959 | -2.26390 |
| H | -4.14604 | -2.34961 | 1.38188 |
| H | -4.00834 | -2.80176 | -1.06066 |
| N | 0.07030 | -0.56574 | 1.46166 |
| O | 0.44666 | -1.29970 | -2.47471 |
| C | 0.39753 | -1.47600 | -1.27513 |
| C | 1.66531 | -1.88569 | -0.52071 |
| H | 1.38787 | -2.39214 | 0.40564 |
| H | 2.16775 | -2.60114 | -1.17627 |
| C | 0.11797 | -0.57990 | 2.91053 |
| H | 1.13905 | -0.35024 | 3.21965 |
| H | -0.55123 | 0.17135 | 3.35824 |
| H | -0.14835 | -1.56494 | 3.30224 |
| O | -0.71895 | 1.84383 | -0.95067 |
| C | -1.92486 | 2.34286 | -0.48105 |
| C | -2.13500 | 3.76202 | -1.03735 |
| H | -1.31536 | 4.40851 | -0.71077 |
| H | -2.12556 | 3.72746 | -2.13034 |
| H | -3.08401 | 4.19986 | -0.70652 |
| C | -1.95498 | 2.41609 | 1.06055 |
| H | -2.90264 | 2.83057 | 1.42099 |
| H | -1.83122 | 1.41563 | 1.48814 |
| H | -1.13844 | 3.04840 | 1.42290 |
| C | -3.09382 | 1.45365 | -0.94281 |
| H | -3.07274 | 1.36706 | -2.03319 |
| H | -2.98386 | 0.45114 | -0.52158 |
| H | -4.06649 | 1.85864 | -0.63844 |

**Product 53** + tert-butanol

47

-981.6845553

| | | | |
|---|---|---|---|
| C | 4.09018 | -0.59050 | -0.58003 |
| C | 2.75878 | -0.60518 | -0.18698 |
| C | 2.16764 | 0.53124 | 0.43141 |
| C | 3.00212 | 1.66835 | 0.57834 |
| C | 4.32515 | 1.67365 | 0.16329 |
| C | 4.89740 | 0.53647 | -0.40860 |
| H | 4.50005 | -1.47520 | -1.06046 |
| H | 2.58014 | 2.55955 | 1.03455 |
| H | 4.92152 | 2.57110 | 0.29809 |
| H | 5.93092 | 0.53233 | -0.73368 |
| C | 0.77345 | 0.57972 | 0.77855 |
| H | 0.51331 | 1.49493 | 1.32055 |
| H | -0.49476 | 1.50131 | -0.54906 |
| C | -0.83623 | -1.29383 | 0.82717 |
| C | -0.69774 | -1.60953 | -0.54570 |
| C | -1.99208 | -1.75029 | 1.49158 |
| C | -1.72575 | -2.25193 | -1.23076 |
| C | -2.99517 | -2.41300 | 0.79349 |
| H | -2.13051 | -1.53853 | 2.54425 |
| C | -2.88440 | -2.65422 | -0.57510 |
| H | -1.58081 | -2.45803 | -2.28595 |
| H | -3.88707 | -2.72509 | 1.32681 |
| H | -3.67662 | -3.16108 | -1.11257 |
| N | 0.15260 | -0.56131 | 1.44447 |
| O | 0.65295 | -1.16566 | -2.43852 |
| C | 0.60106 | -1.41196 | -1.24870 |
| C | 1.87991 | -1.79210 | -0.49184 |
| H | 1.60581 | -2.32822 | 0.41967 |
| H | 2.41475 | -2.47930 | -1.15365 |
| C | 0.16249 | -0.51427 | 2.89617 |
| H | 1.15438 | -0.19464 | 3.21611 |
| H | -0.57204 | 0.20327 | 3.29467 |
| H | -0.04273 | -1.49832 | 3.32795 |
| O | -1.04709 | 2.17305 | -1.01775 |
| C | -2.33560 | 2.26551 | -0.42802 |
| C | -2.90362 | 3.60863 | -0.87869 |
| H | -2.26603 | 4.42219 | -0.52444 |
| H | -2.93829 | 3.64850 | -1.97017 |
| H | -3.91464 | 3.75530 | -0.48917 |
| C | -2.24025 | 2.21839 | 1.09912 |
| H | -3.22586 | 2.37027 | 1.54886 |
| H | -1.85793 | 1.24712 | 1.42566 |
| H | -1.56409 | 2.99780 | 1.46072 |
| C | -3.22406 | 1.12338 | -0.92544 |
| H | -3.26000 | 1.13058 | -2.01777 |
| H | -2.82136 | 0.16176 | -0.60062 |
| H | -4.24276 | 1.22128 | -0.53712 |




53 S46

**SM 53**

32

-748.0309499

| | | | |
|---|---|---|---|
| C | 3.10684 | -0.96942 | 0.92380 |
| C | 1.87035 | -0.44529 | 0.58343 |
| C | 1.75326 | 0.60474 | -0.38501 |
| C | 2.97397 | 1.00630 | -1.00766 |
| C | 4.19599 | 0.45658 | -0.66160 |
| C | 4.29387 | -0.52621 | 0.32916 |
| H | 3.14281 | -1.78061 | 1.64743 |
| H | 2.93008 | 1.78215 | -1.76728 |
| H | 5.09414 | 0.80718 | -1.16272 |
| H | 5.24882 | -0.95858 | 0.60135 |
| C | 0.50456 | 1.12710 | -0.78450 |
| H | 0.51981 | 1.87900 | -1.57717 |
| C | -1.74189 | 0.62946 | 0.07490 |
| C | -1.65468 | -0.76256 | -0.15976 |
| C | -3.02356 | 1.19419 | 0.21422 |
| C | -2.80525 | -1.51594 | -0.36750 |
| C | -4.16265 | 0.41730 | 0.02821 |
| H | -3.13214 | 2.25210 | 0.41529 |
| C | -4.06843 | -0.93641 | -0.28555 |
| H | -2.69067 | -2.57767 | -0.55887 |
| H | -5.13769 | 0.88620 | 0.11218 |
| H | -4.96056 | -1.53090 | -0.44036 |
| N | -0.57296 | 1.35702 | 0.15522 |
| O | -0.11182 | -2.47544 | -0.69248 |
| C | -0.34765 | -1.47236 | -0.04480 |
| C | 0.59636 | -1.06634 | 1.09782 |
| H | 0.06131 | -0.40090 | 1.77924 |
| H | 0.83001 | -1.99526 | 1.62639 |
| C | -0.65829 | 2.71355 | 0.67031 |
| H | 0.34813 | 3.03504 | 0.93604 |
| H | -1.05796 | 3.41824 | -0.07568 |
| H | -1.28753 | 2.76014 | 1.56459 |

**TS** of **53** cyclising to form **S46**

32

-748.0303177

| | | | |
|---|---|---|---|
| C | 3.10343 | -0.97492 | 1.01492 |
| C | 1.86914 | -0.51582 | 0.58441 |
| C | 1.76747 | 0.51554 | -0.39083 |
| C | 2.98252 | 0.98655 | -0.94384 |
| C | 4.21396 | 0.50143 | -0.51980 |
| C | 4.29399 | -0.46755 | 0.48069 |
| H | 3.14119 | -1.77983 | 1.74457 |
| H | 2.94078 | 1.75652 | -1.70933 |
| H | 5.12380 | 0.89324 | -0.96498 |
| H | 5.25334 | -0.84705 | 0.81240 |
| C | 0.47357 | 0.91207 | -0.85982 |
| H | 0.48474 | 1.57412 | -1.73321 |
| C | -1.74446 | 0.64648 | 0.09179 |
| C | -1.69120 | -0.73848 | -0.18318 |
| C | -2.99725 | 1.23215 | 0.33459 |
| C | -2.85728 | -1.47659 | -0.31206 |
| C | -4.15914 | 0.46735 | 0.22194 |
| H | -3.07605 | 2.28737 | 0.56277 |
| C | -4.10567 | -0.87966 | -0.11901 |
| H | -2.77266 | -2.53440 | -0.53910 |
| H | -5.11965 | 0.94548 | 0.38477 |
| H | -5.01560 | -1.45979 | -0.21553 |
| N | -0.54505 | 1.32461 | 0.08794 |
| O | -0.14122 | -2.37845 | -0.93540 |
| C | -0.35533 | -1.40947 | -0.21781 |
| C | 0.57151 | -1.15169 | 0.99413 |
| H | 0.03395 | -0.52975 | 1.71474 |
| H | 0.75275 | -2.13047 | 1.44919 |
| C | -0.55806 | 2.73135 | 0.44630 |
| H | 0.47301 | 3.05559 | 0.58391 |
| H | -1.01641 | 3.35390 | -0.33860 |
| H | -1.10137 | 2.89796 | 1.38152 |

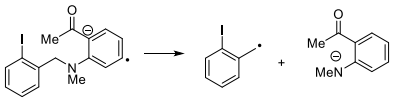
**Product S46**

32

-748.0629296

| | | | |
|---|---|---|---|
| C | -3.11022 | -1.12742 | -1.05971 |
| C | -1.87379 | -0.81536 | -0.50848 |
| C | -1.74976 | 0.29071 | 0.34256 |
| C | -2.85381 | 1.06977 | 0.66061 |
| C | -4.09539 | 0.75642 | 0.10194 |
| C | -4.21956 | -0.33404 | -0.75497 |
| H | -3.21896 | -1.98844 | -1.71161 |
| H | -2.75810 | 1.90542 | 1.34730 |
| H | -4.96661 | 1.35489 | 0.34478 |
| H | -5.18853 | -0.57793 | -1.17713 |
| C | -0.33003 | 0.41292 | 0.81295 |
| H | -0.23459 | 0.72302 | 1.86391 |
| C | 1.74671 | 0.69518 | -0.17801 |
| C | 1.70354 | -0.66111 | 0.17971 |
| C | 2.93830 | 1.29453 | -0.57913 |
| C | 2.84990 | -1.42478 | 0.14250 |
| C | 4.09141 | 0.50011 | -0.63226 |
| H | 2.98736 | 2.34716 | -0.83391 |
| C | 4.05717 | -0.84327 | -0.27607 |
| H | 2.80545 | -2.46247 | 0.45876 |
| H | 5.02885 | 0.95146 | -0.93997 |
| H | 4.96616 | -1.43371 | -0.30654 |
| N | 0.48294 | 1.27827 | -0.06194 |
| O | 0.16022 | -1.87163 | 1.64216 |
| C | 0.28194 | -1.04500 | 0.60903 |
| C | -0.54986 | -1.51438 | -0.66283 |
| H | -0.07859 | -1.20337 | -1.60356 |
| H | -0.62841 | -2.60323 | -0.64909 |
| C | 0.37955 | 2.70527 | 0.13166 |
| H | -0.67463 | 2.98898 | 0.12762 |
| H | 0.82975 | 3.02895 | 1.08407 |
| H | 0.87196 | 3.23707 | -0.68536 |

## 10 Possible CN cleavage in DMSO Scheme 4.2




56 S52 S53

**TS** of CN cleavage of **56**

35

-760.5905567

| | | | |
|---|---|---|---|
| C | -2.69899 | 3.29057 | 0.44189 |
| C | -1.56304 | 2.77252 | -0.14371 |
| C | -1.38412 | 1.37302 | -0.38558 |
| C | -2.47975 | 0.56034 | 0.02461 |
| C | -3.62596 | 1.07187 | 0.60414 |
| C | -3.74944 | 2.44805 | 0.83291 |
| H | -2.77710 | 4.36097 | 0.60035 |
| H | -4.43691 | 0.40774 | 0.87866 |
| H | -4.64537 | 2.84312 | 1.29442 |
| C | -0.12108 | 0.91790 | -0.86280 |
| H | -0.01755 | -0.12208 | -1.15233 |
| H | 0.43624 | 1.62018 | -1.47291 |
| C | 2.42582 | 0.83986 | 0.12344 |
| C | 3.32954 | -0.28398 | 0.19932 |
| C | 2.95471 | 2.03232 | -0.47079 |
| C | 4.70526 | -0.07073 | -0.05602 |
| C | 4.28131 | 2.17427 | -0.78782 |
| H | 2.26753 | 2.86322 | -0.59834 |
| C | 5.19398 | 1.12355 | -0.53834 |
| H | 5.39346 | -0.89962 | 0.07036 |
| H | 4.63693 | 3.11155 | -1.20342 |
| H | 6.24851 | 1.24307 | -0.75333 |
| N | 1.15747 | 0.92742 | 0.58405 |
| O | 1.79165 | -2.05985 | -0.08607 |
| C | 2.88953 | -1.67592 | 0.31864 |
| C | 3.85494 | -2.71299 | 0.87274 |
| H | 4.50702 | -2.31284 | 1.64876 |
| H | 3.26949 | -3.54094 | 1.27113 |
| C | 0.66616 | -0.02985 | 1.55091 |
| H | 0.33835 | -0.97757 | 1.11412 |
| H | 1.44697 | -0.26173 | 2.28781 |
| H | -0.18385 | 0.42059 | 2.07303 |
| H | -0.75451 | 3.43594 | -0.43557 |
| H | 4.48273 | -3.10521 | 0.06718 |
| I | -2.46643 | -1.54876 | -0.36662 |

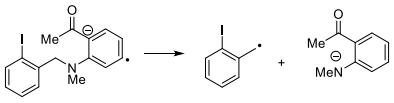
**Products** of CN cleavage **S52** and **S53**

35

-760.6046657

| | | | |
|---|---|---|---|
| C | 2.03457 | 3.37251 | -0.60934 |
| C | 1.57725 | 2.80456 | 0.56216 |
| C | 1.78436 | 1.43099 | 0.86935 |
| C | 2.50108 | 0.67947 | -0.09891 |
| C | 2.96030 | 1.24348 | -1.27572 |
| C | 2.72767 | 2.59429 | -1.53888 |
| H | 1.85079 | 4.42166 | -0.80771 |
| H | 3.49707 | 0.64012 | -1.99676 |
| H | 3.08909 | 3.02746 | -2.46347 |
| C | 1.25232 | 0.90486 | 2.06237 |
| H | 1.36673 | -0.13314 | 2.33622 |
| H | 0.70446 | 1.55399 | 2.73185 |
| C | -2.94097 | 0.81897 | 0.07546 |
| C | -3.43638 | -0.52136 | -0.24841 |
| C | -3.93621 | 1.70590 | 0.66076 |
| C | -4.83975 | -0.72302 | -0.34456 |
| C | -5.27123 | 1.43362 | 0.61647 |
| H | -3.57480 | 2.64770 | 1.06213 |
| C | -5.75699 | 0.22047 | 0.04926 |
| H | -5.20316 | -1.68902 | -0.68050 |
| H | -5.97708 | 2.15728 | 1.01388 |
| H | -6.82004 | 0.02336 | -0.00887 |
| N | -1.75834 | 1.33035 | -0.17006 |
| O | -1.51175 | -1.74982 | 0.37856 |
| C | -2.58998 | -1.69807 | -0.22658 |
| C | -3.07670 | -2.97630 | -0.90157 |
| H | -3.64371 | -2.78535 | -1.81279 |
| H | -2.20475 | -3.58660 | -1.13488 |
| C | -0.82249 | 0.60286 | -0.99029 |
| H | -0.24652 | -0.14823 | -0.43648 |
| H | -1.32659 | 0.05519 | -1.80599 |
| H | -0.11000 | 1.31076 | -1.42664 |
| H | 1.02835 | 3.40442 | 1.27971 |
| H | -3.71190 | -3.54588 | -0.21717 |
| I | 2.88082 | -1.39674 | 0.19925 |

## 11 Possible CN cleavage in Benzene Scheme 4.2




56 S52 S53

**TS** of CN cleavage of **56**

35
-760.5585428

| | | | |
|---|---|---|---|
| C | -2.70397 | 3.28389 | 0.45696 |
| C | -1.56839 | 2.76966 | -0.12993 |
| C | -1.39203 | 1.37263 | -0.38743 |
| C | -2.48769 | 0.55802 | 0.01905 |
| C | -3.63344 | 1.06584 | 0.60031 |
| C | -3.75802 | 2.44055 | 0.83709 |
| H | -2.77811 | 4.35273 | 0.62861 |
| H | -4.44243 | 0.39783 | 0.87083 |
| H | -4.65433 | 2.83328 | 1.30014 |
| C | -0.13560 | 0.92049 | -0.87763 |
| H | -0.02719 | -0.11876 | -1.16754 |
| H | 0.42339 | 1.62569 | -1.48216 |
| C | 2.42310 | 0.83942 | 0.11761 |
| C | 3.33298 | -0.27965 | 0.20612 |
| C | 2.95034 | 2.02886 | -0.48757 |
| C | 4.70720 | -0.06250 | -0.04623 |
| C | 4.27700 | 2.17378 | -0.79739 |
| H | 2.25830 | 2.85425 | -0.62234 |
| C | 5.19436 | 1.12996 | -0.53467 |
| H | 5.39816 | -0.88808 | 0.08844 |
| H | 4.63041 | 3.10974 | -1.21862 |
| H | 6.24955 | 1.25250 | -0.74551 |
| N | 1.15907 | 0.92685 | 0.57433 |
| O | 1.79293 | -2.05891 | -0.06010 |
| C | 2.89142 | -1.67135 | 0.32687 |
| C | 3.86787 | -2.71067 | 0.86854 |
| H | 4.51137 | -2.31591 | 1.65517 |
| H | 3.28454 | -3.54840 | 1.24894 |
| C | 0.66144 | -0.02003 | 1.54608 |
| H | 0.33576 | -0.97277 | 1.11770 |
| H | 1.43921 | -0.24409 | 2.28922 |
| H | -0.19067 | 0.43936 | 2.05709 |
| H | -0.75279 | 3.43106 | -0.40511 |
| H | 4.50299 | -3.08315 | 0.05947 |
| I | -2.46046 | -1.55048 | -0.36831 |

**Products** of CN cleavage **S52** and **S53**

35
-760.5719419

| | | | |
|---|---|---|---|
| C | -1.59237 | 3.07639 | 0.62609 |
| C | -0.82792 | 1.96219 | 0.34530 |
| C | -1.42238 | 0.70236 | 0.03872 |
| C | -2.84218 | 0.66987 | 0.03822 |
| C | -3.60974 | 1.78629 | 0.31922 |
| C | -2.98759 | 2.99908 | 0.61696 |
| H | -1.10269 | 4.01573 | 0.85572 |
| H | -4.69036 | 1.72067 | 0.30942 |
| H | -3.59296 | 3.86976 | 0.83897 |
| C | -0.58211 | -0.39552 | -0.22917 |
| H | -0.98177 | -1.37424 | -0.45222 |
| H | 0.49416 | -0.27807 | -0.18773 |
| C | 3.35232 | 0.79831 | -0.06078 |
| C | 4.06928 | -0.46380 | 0.13347 |
| C | 3.83033 | 1.60115 | -1.17620 |
| C | 5.34473 | -0.61961 | -0.47169 |
| C | 5.02889 | 1.36703 | -1.77977 |
| H | 3.22386 | 2.45870 | -1.44974 |
| C | 5.84850 | 0.26916 | -1.38950 |
| H | 5.91933 | -1.51305 | -0.24812 |
| H | 5.36946 | 2.03408 | -2.56662 |
| H | 6.81437 | 0.10685 | -1.85196 |
| N | 2.40305 | 1.31967 | 0.67705 |
| O | 2.20835 | -1.78994 | 0.75530 |
| C | 3.43191 | -1.64362 | 0.68453 |
| C | 4.30311 | -2.82194 | 1.11985 |
| H | 5.21723 | -2.50714 | 1.62491 |
| H | 3.70800 | -3.44555 | 1.78595 |
| C | 2.07189 | 0.72445 | 1.94667 |
| H | 1.32630 | -0.07919 | 1.87231 |
| H | 2.94837 | 0.27494 | 2.44224 |
| H | 1.66511 | 1.50403 | 2.59998 |
| H | 0.26002 | 2.00828 | 0.35231 |
| H | 4.58314 | -3.42406 | 0.25073 |
| I | -3.88962 | -1.13888 | -0.40621 |